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(54) Title: DETERGENT TABLET			
(57) Abstract			
<p>The present invention provides a detergent tablet comprising a compressed portion and a non-compressed portion wherein: a) the compressed portion comprises compressed detergent components and a cavity extending from a first exterior surface of the compressed portion to a second exterior surface of the compressed portion; and b) the non-compressed portion is retained within said cavity.</p>			

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Detergent TabletTechnical Field

The present invention relates to a detergent tablet comprising a compressed portion comprising compressed detergent components and a cavity and a non-compressed portion wherein the non-compressed portion is retained within the cavity provided by the compressed portion.

Background

Detergent compositions in tablet form are known in the art. It is understood that detergent compositions in tablet form hold several advantages over detergent compositions in particulate form, such as ease of handling, transportation and storage.

Detergent tablets are most commonly prepared by pre-mixing components of a detergent composition and forming the pre-mixed detergent components into a tablet using a tablet press. Tablets are typically formed by compression of the detergent components into a tablet. However, the Applicant has found that some components of a detergent composition are adversely affected by the compression pressure used to form the tablets. These components could not previously be included in a detergent tablet composition without sustaining a loss in performance. In some cases the components may even have become unstable or inactive as a result of the compression.

Furthermore as the components of the detergent composition are compressed, the components are brought into close proximity with each other. A result of the close proximity of the components can be that certain of the components react with each other, becoming unstable, inactive or exhausted. A solution to this problem, as seen in the prior art, has been to separate detergent components that may potentially react with each, especially when the components are compressed into tablet form. Separation of the components has been achieved by, for example, preparing multiple-layer tablets wherein the components that may potentially react with each other are contained in different layers of the tablet. Multiple-layer tablets, are traditionally prepared using multiple compression steps. Layers of the tablet that are subjected to more than one compression step are subjected to a cumulative and potentially greater overall compression pressure.

An increase in compression pressure is known to decrease the rate of dissolution of the tablet with the effect that such multiple layer may not dissolve satisfactorily in use.

Other methods of achieving separation of detergent components have been described. For example EP-A 0,224,135 describes a dishwashing detergent in a form which comprises a warm water-soluble melt, into which is pressed a cold water-soluble tablet. The document teaches a detergent composition that consists of two parts, the first part dissolving in the pre-rinse and the second part dissolving in the main wash of the dishwasher.

EP-B-0,055,100 describes a lavatory block formed by combining a slow dissolving shaped body with a tablet. The lavatory block is designed to be placed in the cistern of a lavatory and dissolves over a period of days, preferably weeks. As a means of controlling the dissolution of the lavatory block, the document teaches admixing one or more solubility control agents. Examples of such solubility control agents are paradichlorobenzene, waxes, long chain fatty acids and alcohols and esters thereof and fatty alkylamides.

The Applicant has found that by providing a detergent tablet comprising a compressed portion and a non-compressed portion detergent components previously considered to be unacceptable for detergent tablets, can be incorporated into a detergent tablet. In addition, potentially reactive components of the detergent composition can be effectively separated.

A further advantage of using a detergent tablet as described herein, is the performance benefits which may be achieved in being able to prepare a detergent tablet that has a faster rate of dissolution versus conventional detergent tablets known in the prior art of equivalent dimensions. It is believed that the performance benefits are achieved because the components of the detergent tablet are delivered to the wash at a faster rate.

Summary of the Invention

According to the present invention there is provided a detergent tablet comprising a compressed portion and a non-compressed portion wherein:

- a) the compressed portion comprises at least one compressed detergent component and a cavity extending from a first external surface of the compressed portion to a second external surface of the compressed portion; and
- b) the non-compressed portion is retained within said cavity.

Detailed Description of the Invention

Compressed portion

The compressed portion of the detergent tablet comprises at least one compressed detergent component, but preferably a comprises a mixture of compressed detergent components. Any detergent component conventionally used in known detergent tablets is suitable for incorporation into the compressed portion of the detergent tablets of this invention. Suitable detergent components are described hereinafter. Preferred detergent components include builder compound, surfactant, bleaching agent, bleach activator, bleach catalyst, enzyme and an alkalinity source.

The detergent components are preferably prepared in particulate form (i.e. powder or granular form) and may be prepared by any known method, for example conventional spray drying, granulation or agglomeration. The detergent component(s) are premixed and then compressed using any equipment suitable for forming compressed tablets, blocks, bricks or briquettes; described in more detail hereafter.

The compressed portion of the present invention is prepared such that it comprises a cavity which extends from one external surface of the compressed portion to a second external surface of the compressed portion. The method of preparation of the compressed portion is described in more detail later.

Non-Compressed Portion

The non-compressed portion of the present invention is retained within a cavity provided by the compressed portion such that it is substantially exposed at a first external surface and a second external surface of the compressed portion. The non-compressed portion may partially, but preferably substantially fills the cavity provided by the compressed portion.

In a preferred aspect of the present invention the compressed portion and the non-compressed portion have different rates of dissolution, more preferably the non-compressed portion dissolves at a faster rate than the compressed portion. The exposure of the non-compressed portion at a first and a second external surface of the compressed portion means that a greater surface area of the components of the non-compressed portion are exposed to the wash water. The exposure of a greater surface area means that the components of the non-compressed portion of the present invention will dissolve and therefore be delivered to the wash water at a faster rate than components of a non-compressed portion that is exposed at only one external surface of the compressed portion or components of a detergent tablet known in the art.

In addition to the above, as the non-compressed portion dissolves it exposes greater surface area of the compressed portion to the wash water resulting in an increase in rate of dissolution of the compressed portion versus detergent tablets known in the art of comparable dimensions. Preferably the non-compressed portion dissolves in water at less than 30°C.

In one aspect of the present invention, the non-compressed portion comprises a first and a second and optionally subsequent non-compressed portions. In this aspect it is preferred that the first non-compressed portion and the second non-compressed and optionally subsequent non-compressed portions have different rates of dissolution.

The non-compressed portion preferably comprises one or more detergent components as described hereinafter. The non-compressed portion and/or components of the non-compressed portion may be in particulate (i.e. powder or granular), gel or liquid form. The non-compressed portion in addition to comprising a detergent component, may also optionally comprise a carrier component.

The non-compressed portion may be delivered to the compressed portion in solid or flowable form. Where the non-compressed portion is in solid form, it is pre-prepared, optionally shaped and then delivered to the compressed portion. The non-compressed portion is then retained within the cavity provided by the compressed portion by, for example adhesion.

The non-compressed portion is preferably delivered to the compressed portion in

flowable form. The non-compressed portion is then retained within the cavity provided by the compressed portion, for example by adhesion, by forming a coating over the non-compressed portion to secure it to the compressed portion or by hardening, for example (i) by cooling to below the melting point when the flowable composition becomes a solidified melt; (ii) by evaporation of a solvent; (iii) by crystallisation; (iv) by polymerisation of a polymeric component of the flowable non-compressed portion; (v) through pseudo-plastic properties where the flowable non-compressed portion comprises a polymer and shear forces are applied to the non-compressed portion; (vi) combining a binding or gelling agent with the flowable non-compressed portion. In an alternative embodiment the flowable non-compressed portion may be an extrudate that is retained within the cavity provided by the compressed portion by for example any of the mechanism described above or by expansion of the extrudate to the parameters of the cavity provided by the compressed portion.

The non-compressed portion may comprise particulates. The particulates may be prepared by any known method, for example conventional spray drying, granulation, encapsulation or agglomeration. Particulates may be retained within the cavity provided by the compressed portion by incorporating a binding agent or by forming a coating layer over the non-compressed portion.

Where the non-compressed portion comprises a solidified melt, the melt is prepared by heating a composition comprising a detergent component and optional carrier component(s) to above its melting point to form a flowable melt. The flowable melt is then poured into the cavity and allowed to cool. As the melt cools it becomes solid, taking the shape of the cavity at ambient temperature. Where the composition comprises one or more carrier components, the carrier component(s) may be heated to above their melting point, and then a detergent component may be added.

Carrier components suitable for preparing a solidified melt are typically non-detergent active components that can be heated to above melting point to form a liquid and cooled to form an intermolecular matrix that can effectively trap detergent components. A preferred carrier component is an organic polymer that is solid at ambient temperature. Preferably the carrier is polyethylene glycol (PEG).

The flowable non-compressed portion may be in a form comprising a dissolved or suspended detergent component. The flowable non-compressed portion may harden over time to form a solid, semi solid or highly viscous liquid by any of the

methods described above. In particular, the flowable non-compressed portion may harden by evaporation of a solvent. Solvents suitable for use herein may include any known solvent in which a binding or gelling agent is soluble. Preferred solvents may be polar or non-polar and may include water, alcohol, (for example ethanol, acetone) and alcohol derivatives. In an alternative embodiment more than one solvent may be used.

The flowable non-compressed portion may comprise one or more binding or gelling agents. Any binding or gelling agent that has the effect of causing the composition to become solid, semi-solid or highly viscous over time is envisaged for use herein. Although not wishing to be bound by theory, it is believed that mechanisms by which the binding or gelling agent causes a non-solid composition to become solid, semi-solid or highly viscous include: chemical reaction (such as chemical cross linking), or effect interaction between two or more components of the flowable compositions either; chemical or physical interaction of the binding agent with a component of the composition.

In a preferred aspect of the present invention the non-compressed portion comprises a gel. In this aspect the gel is delivered to the cavity provided by the compressed portion of the detergent tablet.

The gel comprises a thickening system and other optional detergent components. In addition the gel may also comprise solid components to aid in the control of the viscosity of the gel in conjunction with the thickening system. Solid components may also act to optionally disrupt the gel thereby aiding dissolution of the gel. When included, the gel portion typically comprises at least 15% solid ingredients, more preferably at least 30% solid components and most preferably at least 40% solid ingredients. However, due to the need to be able to pump or otherwise process the gel, the gel typically does not include more than 90% solid ingredients.

As noted earlier, the gel comprises a thickening system to provide the required viscosity or thickness of the gel. The thickening system typically comprises a non-aqueous liquid diluent and an organic or polymeric gelling additive:

a) Liquid Diluent: the term "solvent" or "diluent" is used herein to connote the liquid portion of the thickening system. While some of the components of the non-

compressed portion may actually dissolve in the "solvent"-containing phase, other components may be present as particulate material dispersed within the "solvent"-containing phase. Thus the term "solvent" is not meant to require that the components of the non-compressed portion be capable of actually dissolving in the solvent. Suitable types of solvents useful in the non-aqueous thickening systems herein include alkylene glycol mono lower alkyl ethers, propylene glycols, ethoxylated or propoxylated ethylene or propylene, glycerol esters, glycerol triacetate, lower molecular weight polyethylene glycols, lower molecular weight methyl esters and amides.

A preferred type of non-aqueous solvent for use herein comprises the mono-, di-, tri-, or tetra- C₂-C₃ alkylene glycol mono C₂-C₆ alkyl ethers. The specific examples of such compounds include diethylene glycol monobutyl ether, tetraethylene glycol monobutyl ether, dipropylene glycol monoethyl ether, and dipropylene glycol monobutyl ether. Diethylene glycol monobutyl ether and dipropylene glycol monobutyl ether are especially preferred. Compounds of the type have been commercially marketed under the tradenames Dowanol, Carbitol, and Cellosolve.

Another preferred type of non-aqueous solvent useful herein comprises the lower molecular weight polyethylene glycols (PEGs). Such materials are those having molecular weights of at least 150. PEGs of molecular weight ranging from 200 to 600 are most preferred.

Yet another preferred type of non-aqueous solvent comprises lower molecular weight methyl esters. Such materials are those of the general formula: R¹-C(O)-OCH₃ wherein R¹ ranges from 1 to 18. Examples of suitable lower molecular weight methyl esters include methyl acetate, methyl propionate, methyl octanoate, and methyl dodecanoate.

The non-aqueous organic solvent(s) employed should, of course, be compatible and non-reactive with components of the non-compressed, e.g. enzymes. Such a solvent component will generally be utilized in an amount of from 10% to 60% by weight of the gel portion. More preferably, the non-aqueous, low-polarity organic solvent will comprise from 20% to 50% by weight of the gel, most preferably from 30% to 50% by weight of the gel.

b) Gelling Additive: a gelling agent or additive is added to the non aqueous solvent of the present invention to complete the thickening system. To form the gel required for suitable phase stability and acceptable rheology of the gel, the organic gelling agent is generally present to the extent of a ratio of solvent to gelling agent in thickening system typically ranging from 99:1 to 1:1. More preferably, the ratios range from 19:1 to 4:1.

The preferred gelling agents of the present invention are selected from castor oil derivatives, polyethylene glycol, sorbitols and related organic thixatropes, organoclays, cellulose and cellulose derivatives, pluronics, stearates and stearate derivatives, sugar/gelatin combination, starches, glycerol and derivatives thereof, organic acid amides such as N-lauryl-L-glutamic acid di-n-butyl amide, polyvinyl pyrrolidone and mixtures thereof.

The preferred gelling agents include castor oil derivatives. Castor oil is a naturally occurring triglyceride obtained from the seeds of *Ricinus Communis*, a plant which grows in most tropical or subtropical areas. The primary fatty acid moiety in the castor oil triglyceride is ricinoleic acid (12-hydroxy oleic acid). It accounts for 90% of the fatty acid moieties. The balance consists of dihydroxystearic, palmitic, stearic, oleic, linoleic, linolenic and eicosanoic moieties. Hydrogenation of the oil (e.g., by hydrogen under pressure) converts the double bonds in the fatty acid moieties to single bonds, thus "hardening" the oil. The hydroxyl groups are unaffected by this reaction.

The resulting hydrogenated castor oil, therefore, has an average of three hydroxyl groups per molecule. It is believed that the presence of these hydroxyl groups accounts in large part for the outstanding structuring properties which are imparted to the gel compared to similar liquid detergent compositions which do not contain castor oil with hydroxyl groups in their fatty acid chains. For use in the detergent tablets of the present invention the castor oil should be hydrogenated to an iodine value of less than 20, and preferably less than 10. Iodine value is a measure of the degree of unsaturation of the oil and is measured by the "Wijis Method," which is well-known in the art. Unhydrogenated castor oil has an iodine value of from 80 to 90.

Hydrogenated castor oil is a commercially available commodity being sold, for example, in various grades under the trademark CASTORWAX.RTM. by NL

Industries, Inc., Highstown, New Jersey. Other Suitable hydrogenated castor oil derivatives are Thixcin R, Thixcin E, Thixatrol ST, Perchem R and Perchem ST, made by Rheox, Laporte. Especially preferred is Thixatrol ST.

Polyethylene glycols when employed as gelling agents, rather than solvents, are low molecular weight materials, having a molecular weight range of from 1000 to 10,000, with 3,000 to 8,000 being the most preferred.

Cellulose and cellulose derivatives when employed in the present invention preferably include: i) Cellulose acetate and Cellulose acetate phthalate (CAP); ii) Hydroxypropyl Methyl Cellulose (HPMC); iii) Carboxymethylcellulose (CMC); and mixtures thereof. The hydroxypropyl methylcellulose polymer preferably has a number average molecular weight of 50,000 to 125,000 and a viscosity of a 2 wt.% aqueous solution at 25°C (ADTMD2363) of 50,000 to 100,000 cps. An especially preferred hydroxypropyl cellulose polymer is Methocel® J75MS-N wherein a 2.0 wt.% aqueous solution at 25°C has a viscosity of about 75,000 cps.

The sugar may be any monosaccharide (e.g. glucose), disaccharide (e.g. sucrose or maltose) or polysaccharide. The most preferred sugar is commonly available sucrose. For the purposes of the present invention type A or B gelatin may be used, available from for example Sigma. Type A gelatin is preferred since it has greater stability in alkaline conditions in comparison to type B. Preferred gelatin also has a bloom strength of between 65 and 300, most preferably between 75 and 100.

The gel may include a variety of detergent components, e.g. enzymes, colourants or structure modifying agents. Structure modifying agents include various polymers and mixtures of polymers included polycarboxylates, carboxymethylcelluloses and starches to aid in adsorption of excess solvent and/or reduce or prevent "bleeding" or leaking of the solvent from the gel, reduce shrinkage or cracking of the gel or aid in the dissolution or breakup of the gel in the wash. In addition, hardness modifying agents may incorporated into the thickening system to adjust the hardness of the gel if desired. These hardness control agents are typically selected from various polymers, such as polyethylene glycol's, polyethylene oxide, polyvinylpyrrolidone, polyvinyl alcohol, hydroxystearic acid and polyacetic acid and when included are typically employed in levels of less than 20% and more preferably less than 10% by weight of the solvent in the thickening system.

The gel is formulated so that it is a pumpable, flowable gel at slightly elevated temperatures of around 30°C or greater to allow increased flexibility in producing the detergent tablet, but becomes highly viscous or hardens at ambient temperatures so that the gel is retained within the cavity provided by the compressed, especially through shipping and handling of the detergent tablet. Such hardening of the gel may be achieved, for example, by (i) cooling to below the flowable temperature of the gel or the removal of shear; (ii) by solvent transfer, for example either to the atmosphere of the compressed portion; or by (iii) by polymerisation of the gelling agent.

Preferably, the gel is formulated such that it hardens sufficiently so that the maximum force needed to push a probe into the non-compressed portion preferably ranges from 0.5N to 40N. This force may be characterised by measuring the maximum force needed to push a probe, fitted with a strain gauge, a set distance into the gel. The set distance may be between 40% and 80% of the total gel depth. This force can be measured on a QTS 25 tester, using a probe of 5 mm diameter. Typical forces measured are in the range of 1N to 25N.

Where the non-compressed portion is an extrudate, the extrudate is prepared by premixing detergent components of the non-compressed portion with optional carrier components to form a viscous paste. The viscous paste is then extruded using any suitable commonly available extrusion equipment such as for example a single or twin screw extruder available from for example APV Baker, Peterborough, U.K. The extrudate is then cut to size either after delivery to the compressed portion, or prior to delivery to the compressed portion of the detergent tablet.

In a preferred embodiment the non-compressed portion is coated with a coating layer. The coating layer may substantially completely encapsulate the detergent tablet or may coat the exposed surfaces of the non-compressed portion. The coating may be used to retain the non-compressed portion within the cavity provided by the compressed portion. This may be particularly advantageous where the non-compressed portion comprises flowable particulates, gels or liquids.

The coating layer preferably comprises a material that becomes solid on contacting the compressed and/or the non-compressed portions within preferably less than 15 minutes, more preferably less than 10 minutes, even more preferably less than 5 minutes, most preferably less than 60 seconds. Preferably the coating layer is water-

soluble. Preferred coating layers comprise materials selected from the group consisting of fatty acids, alcohols, diols, esters and ethers, adipic acid, carboxylic acid, dicarboxylic acid, polyvinyl acetate (PVA), polyvinyl pyrrolidone (PVP), polyacetic acid (PLA), polyethylene glycol (PEG) and mixtures thereof. Preferred carboxylic or dicarboxylic acids preferably comprise an even number of carbon atoms. Preferably carboxylic or dicarboxylic acids comprise at least 4, more preferably at least 6, even more preferably at least 8 carbon atoms, most preferably between 8 and 13 carbon atoms. Preferred dicarboxylic acids include adipic acid, suberic acid, azelaic acid, subacic acid, undecanedioic acid, dodecanoic acid, tridecanedioic and mixtures thereof. Preferred fatty acids are those having a carbon chain length of from C12 to C22, most preferably from C18 to C22. The coating layer may also preferably comprise a disrupting agent. Where present the coating layer generally present at a level of at least 0.05%, preferably at least 0.1%, more preferably at least 1%, most preferably at least 2% or even at least 5% of the detergent tablet.

As an alternative embodiment the coating layer may encapsulate the detergent tablet. In this embodiment the coating layer is present at a level of at least 4%, more preferably at least 5%, most preferably at least 10% of the detergent tablet.

In a preferred embodiment the compressed and/or non-compressed portions and/or coating layer additionally comprise a disrupting agent. The disrupting agent may be a disintegrating or effervescent agent. Suitable disintegrating agents include agents that swell on contact with water or facilitate water influx and/or efflux by forming channels in compressed and/or non-compressed portions. Any known disintegrating or effervescent agent suitable for use in laundry or dishwashing applications is envisaged for use herein. Suitable disintegrating agents include starch, starch derivatives, alginates, carboxymethylcellulose (CMC), CMC-based polymers, sodium acetate, aluminium oxide. Suitable effervescent agents are those that produce a gas on contact with water. Suitable effervescent agents may be oxygen, nitrogen dioxide or carbon dioxide evolving species. Examples of preferred effervescent agents may be selected from the group consisting of perborate, percarbonate, carbonate, bicarbonate and carboxylic acids such as citric or maleic acid.

The detergent tablet of the present invention is manufactured in accordance to a process described herein.

Process

According to the present invention there is also provided a process for preparing a detergent tablet comprising the steps of:

- a) compressing detergent components to form a compressed portion having a cavity extending from a first external surface of the compressed portion to a second external surface of the compressed portion; and
- b) delivering a non-compressed portion to said cavity.

The compressed portion is prepared by pre-mixing a composition of detergent components in a suitable mixer; for example a pan mixer, rotary drum, vertical blender or high shear mixer. Preferably dry particulate components are admixed in a mixer, as described above, and liquid components are applied to the dry particulate components by, for example spraying the liquid components directly onto the dry particulate components. The resulting composition is then formed into a compressed portion in a compression step using any known suitable equipment. Preferably the composition is formed into a compressed portion using a suitable tablet press, wherein the tablet is prepared by compression of the composition between an upper and a lower punch.

The tablet press suitable for preparation of the compressed portion of the present invention is modified such that it is suitable for preparing a compressed portion comprising a cavity extending from one external surface to a second external surface of the compressed portion. The modified tablet press comprises modified upper and/or lower punches.

In a preferred embodiment of the present invention the composition is delivered into a punch cavity of a tablet press and compressed to form a compressed portion using a pressure of preferably greater than 6.3KN/cm², more preferably greater than 9KN/cm², most preferably greater than 14.4KN/cm².

Where the non-compressed portion comprises one or more detergent component the components are pre-mixed using any known suitable mixing equipment. The non-compressed portion may be prepared in solid or flowable form. Once prepared the composition is delivered to the cavity provided by the compressed portion. The non-compressed portion may be delivered to the compressed portion by manual delivery or

using a nozzle feeder or extruder, more preferably a loss in weight screw feeder available from Optima, Germany.

Where the flowable non-compressed portion is in particulate form the process comprises delivering a flowable non-compressed portion to the compressed portion in a delivery step and then coating at least a portion of the non-compressed portion with a coating layer such that the coating layer has the effect of substantially retaining the non-compressed portion within the cavity provided by the compressed portion.

Where the flowable non-compressed portion is affixed to and retaining within the cavity provided by the compressed portion by hardening (e.g. a gel), the process comprises a delivery step in which the flowable non-compressed portion is delivered to the compressed portion and a subsequent conditioning step, wherein the non-compressed portion hardens. Such a conditioning step may comprise drying, cooling, binding, polymerisation etc. of the non-compressed portion, during which the non-compressed portion becomes solid, semi-solid or highly viscous. Heat may be used in a drying step. Heat, or exposure to radiation may be used to effect polymerisation in a polymerisation step.

It is also envisaged that the compressed portion may be prepared having a plurality of cavities. The plurality of cavities are then filled with a non-compressed portion. It is also envisaged that each cavity may be filled with a different non-compressed portion or alternatively, each cavity can be filled with a plurality of different non-compressed portions.

Detergent Components

The compressed portion of the detergent tablets described herein comprises compressed detergent components. Suitable detergent components may include a variety of different detergent components commonly used in detergent compositions including builder compounds, surfactants, enzymes, bleaching agents, alkalinity sources, colourants, perfume, lime soap dispersants, organic polymeric compounds including polymeric dye transfer inhibiting agents, crystal growth inhibitors, heavy metal ion sequestrants, metal ion salts, enzyme stabilisers, corrosion inhibitors, suds suppressers, solvents, fabric softening agents, optical brighteners and hydrotropes. In a preferred aspect of the present invention, the non-compressed portion of the detergent tablet also comprises one or more

detergent component. In a particularly preferred aspect of the present invention, the non-compressed portion additionally comprises one or more enzymes, examples of which are described herein.

Highly preferred detergent components include a builder compound, a surfactant, an enzyme and a bleaching agent.

Builder compound

The detergent tablets of the present invention preferably contain a builder compound, typically present at a level of from 1% to 80% by weight, preferably from 10% to 70% by weight, most preferably from 20% to 60% by weight of the composition of active detergent components.

Water-soluble builder compound

Suitable water-soluble builder compounds include the water soluble monomeric polycarboxylates, or their acid forms, homo or copolymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxylic radicals separated from each other by not more than two carbon atoms, carbonates, bicarbonates, borates, phosphates, and mixtures of any of the foregoing.

The carboxylate or polycarboxylate builder can be monomeric or oligomeric in type although monomeric polycarboxylates are generally preferred for reasons of cost and performance.

Suitable carboxylates containing one carboxy group include the water soluble salts of lactic acid, glycolic acid and ether derivatives thereof. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates and the sulfinyl carboxylates. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in British Patent No. 1,389,732, and aminosuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials

such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,439,000.

Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylates, cyclopentadienide pentacarboxylates, 2,3,4,5-tetrahydrofuran - cis, cis, cis-tetracarboxylates, 2,5-tetrahydrofuran - cis - dicarboxylates, 2,2,5,5-tetrahydrofuran - tetracarboxylates, 1,2,3,4,5,6-hexane - hexacarboxylates and carboxymethyl derivatives of polyhydric alcohols such as sorbitol, mannitol and xylitol. Aromatic polycarboxylates include mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in British Patent No. 1,425,343.

Of the above, the preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

The parent acids of the monomeric or oligomeric polycarboxylate chelating agents or mixtures thereof with their salts, e.g. citric acid or citrate/citric acid mixtures are also contemplated as useful builder components.

Borate builders, as well as builders containing borate-forming materials that can produce borate under detergent storage or wash conditions can also be used but are not preferred at wash conditions less than 50°C, especially less than 40°C.

Examples of carbonate builders are the alkaline earth and alkali metal carbonates, including sodium carbonate and sesqui-carbonate and mixtures thereof with ultra-fine calcium carbonate as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

Highly preferred builder compounds for use in the present invention are water-soluble phosphate builders. Specific examples of water-soluble phosphate builders are the

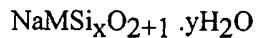
alkali metal tripolyphosphates, sodium, potassium and ammonium pyrophosphate, sodium and potassium and ammonium pyrophosphate, sodium and potassium orthophosphate, sodium polymeta/phosphate in which the degree of polymerisation ranges from 6 to 21, and salts of phytic acid.

Specific examples of water-soluble phosphate builders are the alkali metal tripolyphosphates, sodium, potassium and ammonium pyrophosphate, sodium and potassium and ammonium pyrophosphate, sodium and potassium orthophosphate, sodium polymeta/phosphate in which the degree of polymerization ranges from 6 to 21, and salts of phytic acid.

Partially soluble or insoluble builder compound

The detergent tablets of the present invention may contain a partially soluble or insoluble builder compound. Partially soluble and insoluble builder compounds are particularly suitable for use in tablets prepared for use in laundry cleaning methods. Examples of partially water soluble builders include the crystalline layered silicates as disclosed for example, in EP-A-0164514, DE-A-3417649 and DE-A-3742043.

Preferred are the crystalline layered sodium silicates of general formula



wherein M is sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20. Crystalline layered sodium silicates of this type preferably have a two dimensional 'sheet' structure, such as the so called δ -layered structure, as described in EP 0 164514 and EP 0 293640.

Methods for preparation of crystalline layered silicates of this type are disclosed in DE-A-3417649 and DE-A-3742043. For the purpose of the present invention, x in the general formula above has a value of 2,3 or 4 and is preferably 2.

The most preferred crystalline layered sodium silicate compound has the formula δ - $\text{Na}_2\text{Si}_2\text{O}_5$, known as NaSKS-6 (trade name), available from Hoechst AG.

The crystalline layered sodium silicate material is preferably present in granular detergent compositions as a particulate in intimate admixture with a solid, water-soluble ionisable material as described in PCT Patent Application No. WO92/18594.

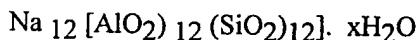
The solid, water-soluble ionisable material is selected from organic acids, organic and inorganic acid salts and mixtures thereof, with citric acid being preferred.

Examples of largely water insoluble builders include the sodium aluminosilicates. Suitable aluminosilicates include the aluminosilicate zeolites having the unit cell formula $\text{Na}_z[(\text{AlO}_2)_z(\text{SiO}_2)_y] \cdot x\text{H}_2\text{O}$ wherein z and y are at least 6; the molar ratio of z to y is from 1.0 to 0.5 and x is at least 5, preferably from 7.5 to 276, more preferably from 10 to 264. The aluminosilicate material are in hydrated form and are preferably crystalline, containing from 10% to 28%, more preferably from 18% to 22% water in bound form.

The aluminosilicate zeolites can be naturally occurring materials, but are preferably synthetically derived. Synthetic crystalline aluminosilicate ion exchange materials are available under the designations Zeolite A, Zeolite B, Zeolite P, Zeolite X, Zeolite HS and mixtures thereof.

A preferred method of synthesizing aluminosilicate zeolites is that described by Schoeman et al (published in Zeolite (1994) 14(2), 110-116), in which the author describes a method of preparing colloidal aluminosilicate zeolites. The colloidal aluminosilicate zeolite particles should preferably be such that no more than 5% of the particles are of size greater than 1 μm in diameter and not more than 5% of particles are of size less than 0.05 μm in diameter. Preferably the aluminosilicate zeolite particles have an average particle size diameter of between 0.01 μm and 1 μm , more preferably between 0.05 μm and 0.9 μm , most preferably between 0.1 μm and 0.6 μm .

Zeolite A has the formula



wherein x is from 20 to 30, especially 27. Zeolite X has the formula $\text{Na}_{86}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \cdot 276\text{H}_2\text{O}$. Zeolite MAP, as disclosed in EP-B-384,070 is a preferred zeolite builder herein.

Preferred aluminosilicate zeolites are the colloidal aluminosilicate zeolites. When employed as a component of a detergent composition colloidal aluminosilicate zeolites, especially colloidal zeolite A, provide enhanced builder performance in terms

of providing improved stain removal. Enhanced builder performance is also seen in terms of reduced fabric encrustation and improved fabric whiteness maintenance; problems believed to be associated with poorly built detergent compositions.

A surprising finding is that mixed aluminosilicate zeolite detergent compositions comprising colloidal zeolite A and colloidal zeolite Y provide equal calcium ion sequestration performance versus an equal weight of commercially available zeolite A. Another surprising finding is that mixed aluminosilicate zeolite detergent compositions, described above, provide improved magnesium ion sequestration performance versus an equal weight of commercially available zeolite A.

Surfactant

Surfactants are preferred detergent active components of the compositions described herein. Suitable surfactants are selected from anionic, cationic, nonionic, ampholytic and zwitterionic surfactants and mixtures thereof. Automatic dishwashing machine products should be low foaming in character and thus the foaming of the surfactant system for use in dishwashing methods must be suppressed or more preferably be low foaming, typically nonionic in character. Sudsing caused by surfactant systems used in laundry cleaning methods need not be suppressed to the same extent as is necessary for dishwashing. The surfactant is typically present at a level of from 0.2% to 30% by weight, more preferably from 0.5% to 10% by weight, most preferably from 1% to 5% by weight of the composition of active detergent components.

A typical listing of anionic, nonionic, ampholytic and zwitterionic classes, and species of these surfactants, is given in U.S.P. 3,929,678 issued to Laughlin and Heuring on December, 30, 1975. A list of suitable cationic surfactants is given in U.S.P. 4,259,217 issued to Murphy on March 31, 1981. A listing of surfactants typically included in automatic dishwashing detergent compositions is given for example, in EP-A-0414 549 and PCT Applications No.s WO 93/08876 and WO 93/08874.

Nonionic surfactant

Essentially any nonionic surfactants useful for detergents purposes can be included in the detergent tablet. Preferred, non-limiting classes of useful nonionic surfactants are listed below.

Nonionic ethoxylated alcohol surfactant

The alkyl ethoxylate condensation products of aliphatic alcohols with from 1 to 25 moles of ethylene oxide are suitable for use herein. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from 6 to 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from 8 to 20 carbon atoms with from 2 to 10 moles of ethylene oxide per mole of alcohol.

End-capped alkyl alkoxylate surfactant

A suitable endcapped alkyl alkoxylate surfactant is the epoxy-capped poly(oxyalkylated) alcohols represented by the formula:



wherein R_1 is a linear or branched, aliphatic hydrocarbon radical having from 4 to 18 carbon atoms; R_2 is a linear or branched aliphatic hydrocarbon radical having from 2 to 26 carbon atoms; x is an integer having an average value of from 0.5 to 1.5, more preferably 1; and y is an integer having a value of at least 15, more preferably at least 20.

Preferably, the surfactant of formula I, at least 10 carbon atoms in the terminal epoxide unit $[CH_2CH(OH)R_2]$. Suitable surfactants of formula I, according to the present invention, are Olin Corporation's POLY-TERGENT® SLF-18B nonionic surfactants, as described, for example, in WO 94/22800, published October 13, 1994 by Olin Corporation.

Ether-capped poly(oxyalkylated) alcohols

Preferred surfactants for use herein include ether-capped poly(oxyalkylated) alcohols having the formula:



wherein R¹ and R² are linear or branched, saturated or unsaturated, aliphatic or aromatic hydrocarbon radicals having from 1 to 30 carbon atoms; R³ is H, or a linear aliphatic hydrocarbon radical having from 1 to 4 carbon atoms; x is an integer having an average value from 1 to 30, wherein when x is 2 or greater R³ may be the same or different and k and j are integers having an average value of from 1 to 12, and more preferably 1 to 5.

R¹ and R² are preferably linear or branched, saturated or unsaturated, aliphatic or aromatic hydrocarbon radicals having from 6 to 22 carbon atoms with 8 to 18 carbon atoms being most preferred. H or a linear aliphatic hydrocarbon radical having from 1 to 2 carbon atoms is most preferred for R³. Preferably, x is an integer having an average value of from 1 to 20, more preferably from 6 to 15.

As described above, when, in the preferred embodiments, and x is greater than 2, R³ may be the same or different. That is, R³ may vary between any of the alklyeneoxy units as described above. For instance, if x is 3, R³ may be selected to form ethlyeneoxy(EO) or propyleneoxy(PO) and may vary in order of (EO)(PO)(EO), (EO)(EO)(PO); (EO)(EO)(EO); (PO)(EO)(PO); (PO)(PO)(EO) and (PO)(PO)(PO). Of course, the integer three is chosen for example only and the variation may be much larger with a higher integer value for x and include, for example, mulitple (EO) units and a much small number of (PO) units.

Particularly preferred surfactants as described above include those that have a low cloud point of less than 20°C. These low cloud point surfactants may then be employed in conjunction with a high cloud point surfactant as described in detail below for superior grease cleaning benefits.

Most preferred ether-capped poly(oxyalkylated) alcohol surfactants are those wherein k is 1 and j is 1 so that the surfactants have the formula:



where R¹, R² and R³ are defined as above and x is an integer with an average value of from 1 to 30, preferably from 1 to 20, and even more preferably from 6 to 18. Most preferred are surfactants wherein R¹ and R² range from 9 to 14, R³ is H forming ethyleneoxy and x ranges from 6 to 15.

The ether-capped poly(oxyalkylated) alcohol surfactants comprise three general components, namely a linear or branched alcohol, an alkylene oxide and an alkyl ether end cap. The alkyl ether end cap and the alcohol serve as a hydrophobic, oil-soluble portion of the molecule while the alkylene oxide group forms the hydrophilic, water-soluble portion of the molecule.

These surfactants exhibit significant improvements in spotting and filming characteristics and removal of greasy soils, when used in conjunction with high cloud point surfactants, relative to conventional surfactants.

Generally speaking, the ether-capped poly(oxyalkylene) alcohol surfactants of the present invention may be produced by reacting an aliphatic alcohol with an epoxide to form an ether which is then reacted with a base to form a second epoxide. The second epoxide is then reacted with an alkoxyLATED alcohol to form the novel compounds of the present invention. Examples of methods of preparing the ether-capped poly(oxyalkylated) alcohol surfactants are described below:

Preparation of C₁₂/14 alkyl glycidyl ether

A C₁₂/14 fatty alcohol (100.00 g, 0.515 mol.) and tin (IV) chloride (0.58 g, 2.23 mmol, available from Aldrich) are combined in a 500 mL three-necked round-bottomed flask fitted with a condenser, argon inlet, addition funnel, magnetic stirrer and internal temperature probe. The mixture is heated to 60 °C. Epichlorhydrin (47.70 g, 0.515 mol, available from Aldrich) is added dropwise so as to keep the temperature between 60-65 °C. After stirring an additional hour at 60 °C, the mixture is cooled to room temperature. The mixture is treated with a 50% solution of sodium hydroxide (61.80 g, 0.773 mol, 50%) while being stirred mechanically. After addition is completed, the mixture is heated to 90 °C for 1.5 h, cooled, and filtered with the aid of ethanol. The filtrate is separated and the organic phase is washed with water (100 mL), dried over MgSO₄, filtered, and concentrated. Distillation of the oil at 100-120 °C (0.1 mm Hg) providing the glycidyl ether as an oil.

Preparation of C₁₂/14 alkyl-C₉/11 ether capped alcohol surfactant

Neodol® 91-8 (20.60 g, 0.0393 mol ethoxylated alcohol available from the Shell chemical Co.) and tin (IV) chloride (0.58 g, 2.23 mmol) are combined in a 250 mL

three-necked round-bottomed flask fitted with a condenser, argon inlet, addition funnel, magnetic stirrer and internal temperature probe. The mixture is heated to 60 °C at which point C₁₂/14 alkyl glycidyl ether (11.00 g, 0.0393 mol) is added dropwise over 15 min. After stirring for 18 h at 60 °C, the mixture is cooled to room temperature and dissolved in an equal portion of dichloromethane. The solution is passed through a 1 inch pad of silica gel while eluting with dichloromethane. The filtrate is concentrated by rotary evaporation and then stripped in a kugelrohr oven (100 °C, 0.5 mm Hg) to yield the surfactant as an oil.

Nonionic ethoxylated/propoxylated fatty alcohol surfactant

The ethoxylated C₆-C₁₈ fatty alcohols and C₆-C₁₈ mixed ethoxylated/propoxylated fatty alcohols are suitable surfactants for use herein, particularly where water soluble. Preferably the ethoxylated fatty alcohols are the C₁₀-C₁₈ ethoxylated fatty alcohols with a degree of ethoxylation of from 3 to 50, most preferably these are the C₁₂-C₁₈ ethoxylated fatty alcohols with a degree of ethoxylation from 3 to 40. Preferably the mixed ethoxylated/propoxylated fatty alcohols have an alkyl chain length of from 10 to 18 carbon atoms, a degree of ethoxylation of from 3 to 30 and a degree of propoxylation of from 1 to 10.

Nonionic EO/PO condensates with propylene glycol

The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are suitable for use herein. The hydrophobic portion of these compounds preferably has a molecular weight of from 1500 to 1800 and exhibits water insolubility. Examples of compounds of this type include certain of the commercially-available Pluronic™ surfactants, marketed by BASF.

Nonionic EO condensation products with propylene oxide/ethylene diamine adducts

The condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine are suitable for use herein. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from 2500 to 3000. Examples of this type of nonionic surfactant include certain of

the commercially available Tetronic™ compounds, marketed by BASF.

Mixed Nonionic Surfactant System

In a preferred embodiment of the present invention the detergent tablet comprises a mixed nonionic surfactant system comprising at least one low cloud point nonionic surfactant and at least one high cloud point nonionic surfactant.

"Cloud point", as used herein, is a well known property of nonionic surfactants which is the result of the surfactant becoming less soluble with increasing temperature, the temperature at which the appearance of a second phase is observable is referred to as the "cloud point" (See Kirk Othmer's Encyclopedia of Chemical Technology, 3rd Ed. Vol. 22, pp. 360-379).

As used herein, a "low cloud point" nonionic surfactant is defined as a nonionic surfactant system component having a cloud point of less than 30°C, preferably less than 20°C, and most preferably less than 10°C. Typical low cloud point nonionic surfactants include nonionic alkoxylated surfactants, especially ethoxylates derived from primary alcohol, and polyoxypropylene/polyoxyethylene/polyoxypropylene (PO/EO/PO) reverse block polymers. Also, such low cloud point nonionic surfactants include, for example, ethoxylated-propoxylated alcohol (e.g., Olin Corporation's Poly-Tergent® SLF18), epoxy-capped poly(oxyalkylated) alcohols (e.g., Olin Corporation's Poly-Tergent® SLF18B series of nonionics, as described, for example, in WO 94/22800, published October 13, 1994 by Olin Corporation) and the ether-capped poly(oxyalkylated) alcohol surfactants.

Nonionic surfactants can optionally contain propylene oxide in an amount up to 15% by weight. Other preferred nonionic surfactants can be prepared by the processes described in U.S. Patent 4,223,163, issued September 16, 1980, Builloty, incorporated herein by reference.

Low cloud point nonionic surfactants additionally comprise a polyoxyethylene, polyoxypropylene block polymeric compound. Block polyoxyethylene-polyoxypropylene polymeric compounds include those based on ethylene glycol, propylene glycol, glycerol, trimethylolpropane and ethylenediamine as initiator reactive hydrogen compound. Certain of the block polymer surfactant compounds

designated PLURONIC®, REVERSED PLURONIC®, and TETRONIC® by the BASF-Wyandotte Corp., Wyandotte, Michigan, are suitable in ADD compositions of the invention. Preferred examples include REVERSED PLURONIC® 25R2 and TETRONIC® 702. Such surfactants are typically useful herein as low cloud point nonionic surfactants.

As used herein, a "high cloud point" nonionic surfactant is defined as a nonionic surfactant system component having a cloud point of greater than 40°C, preferably greater than 50°C, and more preferably greater than 60°C. Preferably the nonionic surfactant system comprises an ethoxylated surfactant derived from the reaction of a monohydroxy alcohol or alkylphenol containing from 8 to 20 carbon atoms, with from 6 to 15 moles of ethylene oxide per mole of alcohol or alkyl phenol on an average basis. Such high cloud point nonionic surfactants include, for example, Tergitol 15S9 (supplied by Union Carbide), Rhodasurf TMD 8.5 (supplied by Rhone Poulenc), and Neodol 91-8 (supplied by Shell).

It is also preferred for purposes of the present invention that the high cloud point nonionic surfactant further have a hydrophile-lipophile balance ("HLB"; see Kirk Othmer hereinbefore) value within the range of from 9 to 15, preferably 11 to 15. Such materials include, for example, Tergitol 15S9 (supplied by Union Carbide), Rhodasurf TMD 8.5 (supplied by Rhone Poulenc), and Neodol 91-8 (supplied by Shell).

Another preferred high cloud point nonionic surfactant is derived from a straight or preferably branched chain or secondary fatty alcohol containing from 6 to 20 carbon atoms (C₆-C₂₀ alcohol), including secondary alcohols and branched chain primary alcohols. Preferably, high cloud point nonionic surfactants are branched or secondary alcohol ethoxylates, more preferably mixed C9/11 or C11/15 branched alcohol ethoxylates, condensed with an average of from 6 to 15 moles, preferably from 6 to 12 moles, and most preferably from 6 to 9 moles of ethylene oxide per mole of alcohol. Preferably the ethoxylated nonionic surfactant so derived has a narrow ethoxylate distribution relative to the average.

In a preferred embodiment the detergent tablet comprising such a mixed surfactant system also comprises an amount of water-soluble salt to provide conductivity in deionised water measured at 25°C greater than 3 milli Siemens/cm, preferably greater

than 4 milli Siemens/cm, most preferably greater than 4.5 milli Siemens/cm as described in co-pending GB Patent Application (attorney docket number CM 1573F).

In another preferred embodiment the mixed surfactant system dissolves in water having a hardness of 1.246mmol/L in any suitable cold-fill automatic dishwasher to provide a solution with a surface tension of less than 4 Dynes/cm² at less than 45°C, preferably less than 40°C, most preferably less than 35°C as described in co-pending U.S. Patent Application (attorney docket number 6252).

In another preferred embodiment the high cloud point and low cloud point surfactants of the mixed surfactant system are separated such that one of either the high cloud point or low cloud point surfactants is present in a first matrix and the other is present in a second matrix as described in co-pending U.S. Patent Application (attorney docket number 6252). For the purposes of the present invention, the first matrix may be a first particulate and the second matrix may be a second particulate. A surfactant may be applied to a particulate by any suitable known method, preferably the surfactant is sprayed onto the particulate. In a preferred aspect the first matrix is the compressed portion and the second matrix is the non-compressed portion of the detergent tablet of the present invention. Preferably the low cloud point surfactant is present in the compressed portion and the high cloud point surfactant is present in the non-compressed portion of the detergent tablet of the present invention.

Anionic surfactant

Essentially any anionic surfactants useful for detergents purposes are suitable. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of the anionic sulfate, sulfonate, carboxylate and sarcosinate surfactants. Anionic sulfate surfactants are preferred.

Other anionic surfactants include the isethionates such as the acyl isethionates, N-acyl taurates, fatty acid amides of methyl tauride, alkyl succinates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C₁₂-C₁₈ monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C₆-C₁₄ diesters), N-acyl sarcosinates. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin

acids present in or derived from tallow oil.

Anionic sulfate surfactant

Anionic sulfate surfactants suitable for use herein include the linear and branched primary and secondary alkyl sulfates, alkyl ethoxysulfates, fatty oleoyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, the C₅-C₁₇ acyl-N-(C₁-C₄ alkyl) and -N-(C₁-C₂ hydroxyalkyl) glucamine sulfates, and sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described herein).

Alkyl sulfate surfactants are preferably selected from the linear and branched primary C₁₀-C₁₈ alkyl sulfates, more preferably the C₁₁-C₁₅ branched chain alkyl sulfates and the C₁₂-C₁₄ linear chain alkyl sulfates.

Alkyl ethoxysulfate surfactants are preferably selected from the group consisting of the C₁₀-C₁₈ alkyl sulfates which have been ethoxylated with from 0.5 to 20 moles of ethylene oxide per molecule. More preferably, the alkyl ethoxysulfate surfactant is a C₁₁-C₁₈, most preferably C₁₁-C₁₅ alkyl sulfate which has been ethoxylated with from 0.5 to 7, preferably from 1 to 5, moles of ethylene oxide per molecule.

A particularly preferred aspect of the invention employs mixtures of the preferred alkyl sulfate and alkyl ethoxysulfate surfactants. Such mixtures have been disclosed in PCT Patent Application No. WO 93/18124.

Anionic sulfonate surfactant

Anionic sulfonate surfactants suitable for use herein include the salts of C₅-C₂₀ linear alkylbenzene sulfonates, alkyl ester sulfonates, C₆-C₂₂ primary or secondary alkane sulfonates, C₆-C₂₄ olefin sulfonates, sulfonated polycarboxylic acids, alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfonates, and any mixtures thereof.

Anionic carboxylate surfactant

Suitable anionic carboxylate surfactants include the alkyl ethoxy carboxylates, the

alkyl polyethoxy polycarboxylate surfactants and the soaps ('alkyl carboxyls'), especially certain secondary soaps as described herein.

Suitable alkyl ethoxy carboxylates include those with the formula $RO(CH_2CH_2O)_xCH_2COO^-M^+$ wherein R is a C₆ to C₁₈ alkyl group, x ranges from 0 to 10, and the ethoxylate distribution is such that, on a weight basis, the amount of material where x is 0 is less than 20 % and M is a cation. Suitable alkyl polyethoxy polycarboxylate surfactants include those having the formula $RO-(CHR_1-CHR_2-O)-R_3$ wherein R is a C₆ to C₁₈ alkyl group, x is from 1 to 25, R₁ and R₂ are selected from the group consisting of hydrogen, methyl acid radical, succinic acid radical, hydroxysuccinic acid radical, and mixtures thereof, and R₃ is selected from the group consisting of hydrogen, substituted or unsubstituted hydrocarbon having between 1 and 8 carbon atoms, and mixtures thereof.

Suitable soap surfactants include the secondary soap surfactants which contain a carboxyl unit connected to a secondary carbon. Preferred secondary soap surfactants for use herein are water-soluble members selected from the group consisting of the water-soluble salts of 2-methyl-1-undecanoic acid, 2-ethyl-1-decanoic acid, 2-propyl-1-nonanoic acid, 2-butyl-1-octanoic acid and 2-pentyl-1-heptanoic acid. Certain soaps may also be included as suds suppressors.

Alkali metal sarcosinate surfactant

Other suitable anionic surfactants are the alkali metal sarcosinates of formula R-CON(R¹)CH₂COOM, wherein R is a C₅-C₁₇ linear or branched alkyl or alkenyl group, R¹ is a C₁-C₄ alkyl group and M is an alkali metal ion. Preferred examples are the myristyl and oleoyl methyl sarcosinates in the form of their sodium salts.

Amphoteric surfactant

Suitable amphoteric surfactants for use herein include the amine oxide surfactants and the alkyl amphocarboxylic acids.

Suitable amine oxides include those compounds having the formula R³(OR⁴)_xN⁰(R⁵)₂ wherein R³ is selected from an alkyl, hydroxyalkyl, acylamidopropoyl and alkyl phenyl group, or mixtures thereof, containing from 8 to

26 carbon atoms; R⁴ is an alkylene or hydroxyalkylene group containing from 2 to 3 carbon atoms, or mixtures thereof; x is from 0 to 5, preferably from 0 to 3; and each R⁵ is an alkyl or hydroxyalkyl group containing from 1 to 3, or a polyethylene oxide group containing from 1 to 3 ethylene oxide groups. Preferred are C₁₀-C₁₈ alkyl dimethylamine oxide, and C₁₀₋₁₈ acylamido alkyl dimethylamine oxide.

A suitable example of an alkyl aphodicarboxylic acid is Miranol(TM) C2M Conc. manufactured by Miranol, Inc., Dayton, NJ.

Zwitterionic surfactant

Zwitterionic surfactants can also be incorporated into the detergent compositions hereof. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. Betaine and sultaine surfactants are exemplary zwitterionic surfactants for use herein.

Suitable betaines are those compounds having the formula R(R')₂N⁺R²COO⁻ wherein R is a C₆-C₁₈ hydrocarbyl group, each R¹ is typically C₁-C₃ alkyl, and R² is a C₁-C₅ hydrocarbyl group. Preferred betaines are C₁₂₋₁₈ dimethyl-ammonio hexanoate and the C₁₀₋₁₈ acylamidopropane (or ethane) dimethyl (or diethyl) betaines.

Complex betaine surfactants are also suitable for use herein.

Cationic surfactants

Cationic ester surfactants used in this invention are preferably water dispersible compound having surfactant properties comprising at least one ester (i.e. -COO-) linkage and at least one cationically charged group. Other suitable cationic ester surfactants, including choline ester surfactants, have for example been disclosed in US Patents No.s 4228042, 4239660 and 4260529.

Suitable cationic surfactants include the quaternary ammonium surfactants selected from mono C₆-C₁₆, preferably C₆-C₁₀ N-alkyl or alkenyl ammonium surfactants wherein the remaining N positions are substituted by methyl, hydroxyethyl or hydroxypropyl groups.

Enzymes

Enzymes can be included as components of the compressed portion of the detergent tablet. In a preferred embodiment of the present invention enzymes are present as components of the non-compressed portion. In a particularly preferred embodiment, enzymes are present as components of the compressed and non-compressed portions.

Where present said enzymes are selected from the group consisting of cellulases, hemicellulases, peroxidases, proteases, gluco-amylases, amylases, xylanases, lipases, phospholipases, esterases, cutinases, pectinases, keratanases, reductases, oxidases, phenoloxidases, lipoxygenases, ligninases, pullulanases, tannases, pentosanases, malanases, β -glucanases, arabinosidases, hyaluronidase, chondroitinase, laccase or mixtures thereof.

Preferred enzymes include protease, amylase, lipase, peroxidases, cutinase and/or cellulase in conjunction with one or more plant cell wall degrading enzymes.

The cellulases usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 12 and an activity above 50 CEVU (Cellulose Viscosity Unit). Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgaard et al, J61078384 and WO96/02653 which disclose fungal cellulases produced respectively from *Humicola insolens*, *Trichoderma*, *Thielavia* and *Sporotrichum*. EP 739 982 describes cellulases isolated from novel *Bacillus* species. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275; DE-OS-2.247.832 and WO95/26398.

Examples of such cellulases are cellulases produced by a strain of *Humicola insolens* (*Humicola grisea* var. *thermoidea*), particularly the *Humicola* strain DSM 1800. Other suitable cellulases are cellulases originated from *Humicola insolens* having a molecular weight of 50KDa, an isoelectric point of 5.5 and containing 415 amino acids; and a ~43kD endoglucanase derived from *Humicola insolens*, DSM 1800, exhibiting cellulase activity; a preferred endoglucanase component has the amino acid sequence disclosed in PCT Patent Application No. WO 91/17243. Also suitable cellulases are the EGIII cellulases from *Trichoderma longibrachiatum* described in WO94/21801, Genencor, published September 29, 1994. Especially suitable cellulases are the

cellulases having color care benefits. Examples of such cellulases are cellulases described in European patent application No. 91202879.2, filed November 6, 1991 (Novo). Carezyme and Celluzyme (Novo Nordisk A/S) are especially useful. See also WO91/17244 and WO91/21801. Other suitable cellulases for fabric care and/or cleaning properties are described in WO96/34092, WO96/17994 and WO95/24471.

Said cellulases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition.

Peroxidase enzymes are used in combination with oxygen sources, e.g. percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching", i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, WO89/09813 and in European Patent application EP No. 91202882.6, filed on November 6, 1991 and EP No. 96870013.8, filed February 20, 1996. Also suitable is the laccase enzyme.

Preferred enhancers are substituted phenothiazine and phenoxyazine 10-Phenothiazinepropionic acid (PPT), 10-ethylphenothiazine-4-carboxylic acid (EPC), 10-phenoxyazinepropionic acid (POP) and 10-methylphenoxyazine (described in WO 94/12621) and substituted syringates (C3-C5 substituted alkyl syringates) and phenols. Sodium percarbonate or perborate are preferred sources of hydrogen peroxide.

Said cellulases and/or peroxidases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition.

Other preferred enzymes that can be included in the detergent compositions of the present invention include lipases. Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in British Patent 1,372,034. Suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase, produced by the microorganism *Pseudomonas fluorescent* IAM 1057.

This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P". Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. Especially suitable lipases are lipases such as M1 Lipase^R and Lipomax^R (Gist-Brocades) and Lipolase^R and Lipolase Ultra^R(Novo) which have found to be very effective when used in combination with the compositions of the present invention. Also suitables are the lipolytic enzymes described in EP 258 068, WO 92/05249 and WO 95/22615 by Novo Nordisk and in WO 94/03578, WO 95/35381 and WO 96/00292 by Unilever.

Also suitable are cutinases [EC 3.1.1.50] which can be considered as a special kind of lipase, namely lipases which do not require interfacial activation. Addition of cutinases to detergent compositions have been described in e.g. WO-A-88/09367 (Genencor); WO 90/09446 (Plant Genetic System) and WO 94/14963 and WO 94/14964 (Unilever).

The lipases and/or cutinases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition.

Suitable proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis* (subtilisin BPN and BPN'). One suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE^R by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include ALCALASE^R, DURAZYM^R and SAVINASE^R from Novo and MAXATASE^R, MAXACAL^R, PROPERASE^R and MAXAPEM^R (protein engineered Maxacal) from Gist-Brocades. Proteolytic enzymes also encompass modified bacterial serine proteases, such as those described in European Patent Application Serial Number 87 303761.8, filed April 28, 1987 (particularly pages 17, 24 and 98), and which is called herein "Protease B", and in European Patent Application 199,404, Venegas, published October 29, 1986, which refers to a modified bacterial serine proteolytic enzyme which is called "Protease A" herein. Suitable is what is called herein "Protease C", which is a variant of an alkaline serine protease from *Bacillus* in which lysine replaced

arginine at position 27, tyrosine replaced valine at position 104, serine replaced asparagine at position 123, and alanine replaced threonine at position 274. Protease C is described in EP 90915958:4, corresponding to WO 91/06637, Published May 16, 1991. Genetically modified variants, particularly of Protease C, are also included herein.

A preferred protease referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in WO95/10591 and in the patent application of C. Ghosh, et al, "Bleaching Compositions Comprising Protease Enzymes" having US Serial No. 08/322,677, filed October 13, 1994.

Also suitable for the present invention are proteases described in patent applications EP 251 446 and WO 91/06637, protease BLAP® described in WO91/02792 and their variants described in WO 95/23221.

See also a high pH protease from *Bacillus* sp. NCIMB 40338 described in WO 93/18140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 92/03529 A to Novo. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 95/07791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 94/25583 to Novo. Other suitable proteases are described in EP 516 200 by Unilever.

Other preferred protease enzymes include protease enzymes which are a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived by replacement of a plurality of amino acid residues of a precursor carbonyl hydrolase with different amino acids, wherein said plurality of amino acid residues replaced in the precursor enzyme correspond to position +210 in combination with one or more of the following residues: +33, +62, +67, +76, +100, +101, +103, +104, +107, +128,

+129, +130, +132, +135, +156, +158, +164, +166, +167, +170, +209, +215, +217, +218 and +222, where the numbered positions correspond to naturally-occurring subtilisin from Bacillus amyloliquefaciens or to equivalent amino acid residues in other carbonyl hydrolases or subtilisins (such as Bacillus lentus subtilisin). Preferred enzymes of this type include those having position changes +210, +76, +103, +104, +156, and +166.

The proteolytic enzymes are incorporated in the detergent compositions of the present invention a level of from 0.0001% to 2%, preferably from 0.001% to 0.2%, more preferably from 0.005% to 0.1% pure enzyme by weight of the composition.

Amylases (α and/or β) can be included for removal of carbohydrate-based stains. WO94/02597, Novo Nordisk A/S published February 03, 1994, describes cleaning compositions which incorporate mutant amylases. See also WO95/10603, Novo Nordisk A/S, published April 20, 1995. Other amylases known for use in cleaning compositions include both α - and β -amylases. α -Amylases are known in the art and include those disclosed in US Pat. no. 5,003,257; EP 252,666; WO/91/00353; FR 2,676,456; EP 285,123; EP 525,610; EP 368,341; and British Patent specification no. 1,296,839 (Novo). Other suitable amylases are stability-enhanced amylases described in WO94/18314, published August 18, 1994 and WO96/05295, Genencor, published February 22, 1996 and amylase variants having additional modification in the immediate parent available from Novo Nordisk A/S, disclosed in WO 95/10603, published April 95. Also suitable are amylases described in EP 277 216, WO95/26397 and WO96/23873 (all by Novo Nordisk).

Examples of commercial α -amylases products are Purafect Ox Am[®] from Genencor and Termamyl[®], Ban[®], Fungamyl[®] and Duramyl[®], all available from Novo Nordisk A/S Denmark. WO95/26397 describes other suitable amylases : α -amylases characterised by having a specific activity at least 25% higher than the specific activity of Termamyl[®] at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadebas[®] α -amylase activity assay. Suitable are variants of the above enzymes, described in WO96/23873 (Novo Nordisk). Other amyloytic enzymes with improved properties with respect to the activity level and the combination of thermostability and a higher activity level are described in WO95/35382.

Preferred amylase enzymes include those described in WO95/26397 and in co-pending application by Novo Nordisk PCT/DK96/00056.

The amylolytic enzymes are incorporated in the detergent compositions of the present invention a level of from 0.0001% to 2%, preferably from 0.00018% to 0.06%, more preferably from 0.00024% to 0.048% pure enzyme by weight of the composition

In a particularly preferred embodiment, detergent tablets of the present invention comprise amylase enzymes, particularly those described in WO95/26397 and co-pending application by Novo Nordisk PCT/DK96/00056 in combination with a complementary amylase.

By "complementary" it is meant the addition of one or more amylase suitable for detergency purposes. Examples of complementary amylases (α and/or β) are described below. WO94/02597 and WO95/10603, Novo Nordisk A/S describe cleaning compositions which incorporate mutant amylases. Other amylases known for use in cleaning compositions include both α - and β -amylases. α -Amylases are known in the art and include those disclosed in US Pat. no. 5,003,257; EP 252,666; WO/91/00353; FR 2,676,456; EP 285,123; EP 525,610; EP 368,341; and British Patent specification no. 1,296,839 (Novo). Other suitable amylases are stability-enhanced amylases described in WO94/18314, and WO96/05295, Genencor and amylase variants having additional modification in the immediate parent available from Novo Nordisk A/S, disclosed in WO 95/10603. Also suitable are amylases described in EP 277 216 (Novo Nordisk). Examples of commercial α -amylases products are Purafect Ox Am[®] from Genencor and Termamyl[®], Ban[®], Fungamyl[®] and Duramyl[®], all available from Novo Nordisk A/S Denmark. WO95/26397 describes other suitable amylases : α -amylases characterised by having a specific activity at least 25% higher than the specific activity of Termamyl[®] at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadebas[®] α -amylase activity assay. Suitable are variants of the above enzymes, described in WO96/23873 (Novo Nordisk). Other amylolytic enzymes with improved properties with respect to the activity level and the combination of thermostability and a higher activity level are described in WO95/35382. Preferred complementary amylases for the present invention are the amylases sold under the tradename Purafect Ox Am[®] described in WO 94/18314, WO96/05295 sold by Genencor; Termamyl[®], Fungamyl[®], Ban[®] and Duramyl[®], all available from Novo Nordisk A/S and Maxamyl[®] by

Gist-Brocades.

Said complementary amylase is generally incorporated in the detergent compositions of the present invention a level of from 0.0001% to 2%, preferably from 0.00018% to 0.06%, more preferably from 0.00024% to 0.048% pure enzyme by weight of the composition. Preferably a weight of pure enzyme ratio of specific amylase to the complementary amylase is comprised between 9:1 to 1:9, more preferably between 4:1 to 1:4, and most preferably between 2:1 and 1:2.

The above-mentioned enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Origin can further be mesophilic or extremophilic (psychrophilic, psychrotrophic, thermophilic, barophilic, alkalophilic, acidophilic, halophilic, etc.). Purified or non-purified forms of these enzymes may be used. Also included by definition, are mutants of native enzymes. Mutants can be obtained e.g. by protein and/or genetic engineering, chemical and/or physical modifications of native enzymes. Common practice as well is the expression of the enzyme via host organisms in which the genetic material responsible for the production of the enzyme has been cloned.

Said enzymes are normally incorporated in the detergent tablet at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition. The enzymes can be added as separate single components (prills, granulates, stabilized liquids, etc... containing one enzyme) or as mixtures of two or more enzymes (e.g. cogranulates).

Other suitable detergent components that can be added are enzyme oxidation scavengers which are described in Copending European Patent application 92870018.6 filed on January 31, 1992. Examples of such enzyme oxidation scavengers are ethoxylated tetraethylene polyamines.

A range of enzyme materials and means for their incorporation into synthetic detergent tablets is also disclosed in WO 9307263 A and WO 9307260 A to Genencor International, WO 8908694 A to Novo, and U.S. 3,553,139, January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. 4,101,457, Place et al, July 18, 1978, and in U.S. 4,507,219, Hughes, March 26, 1985. Enzyme materials useful for liquid detergent formulations, and their incorporation into such

formulations, are disclosed in U.S. 4,261,868, Hora et al, April 14, 1981. Enzymes for use in detergents can be stabilised by various techniques. Enzyme stabilisation techniques are disclosed and exemplified in U.S. 3,600,319, August 17, 1971, Gedge et al, EP 199,405 and EP 200,586, October 29, 1986, Venegas. Enzyme stabilisation systems are also described, for example, in U.S. 3,519,570. A useful *Bacillus*, sp. AC13 giving proteases, xylanases and cellulases, is described in WO 9401532 A to Novo.

Bleaching agent

A highly preferred component of the detergent tablet is a bleaching agent. Suitable bleaching agents include chlorine and oxygen-releasing bleaching agents.

In one preferred aspect the oxygen-releasing bleaching agent contains a hydrogen peroxide source and an organic peroxyacid bleach precursor compound. The production of the organic peroxyacid occurs by an in situ reaction of the precursor with a source of hydrogen peroxide. Preferred sources of hydrogen peroxide include inorganic perhydrate bleaches. In an alternative preferred aspect a preformed organic peroxyacid is incorporated directly into the composition. Compositions containing mixtures of a hydrogen peroxide source and organic peroxyacid precursor in combination with a preformed organic peroxyacid are also envisaged.

Inorganic perhydrate bleaches

The detergent tablet of the present invention preferably includes a hydrogen peroxide source, as an oxygen-releasing bleach. Suitable hydrogen peroxide sources include the inorganic perhydrate salts.

The inorganic perhydrate salts are normally incorporated in the form of the sodium salt at a level of from 1% to 40% by weight, more preferably from 2% to 30% by weight and most preferably from 5% to 25% by weight of the compositions.

Examples of inorganic perhydrate salts include perborate, percarbonate, perphosphate, persulfate and persilicate salts. The inorganic perhydrate salts are normally the alkali metal salts. The inorganic perhydrate salt may be included as the crystalline solid without additional protection. For certain perhydrate salts however,

the preferred executions of such granular compositions utilize a coated form of the material which provides better storage stability for the perhydrate salt in the granular product.

Sodium perborate can be in the form of the monohydrate of nominal formula $\text{NaBO}_2\text{H}_2\text{O}_2$ or the tetrahydrate $\text{NaBO}_2\text{H}_2\text{O}_2\cdot 3\text{H}_2\text{O}$.

Alkali metal percarbonates, particularly sodium percarbonate are preferred perhydrates for inclusion in compositions in accordance with the invention. Sodium percarbonate is an addition compound having a formula corresponding to $2\text{Na}_2\text{CO}_3\cdot 3\text{H}_2\text{O}_2$, and is available commercially as a crystalline solid. Sodium percarbonate, being a hydrogen peroxide addition compound tends on dissolution to release the hydrogen peroxide quite rapidly which can increase the tendency for localised high bleach concentrations to arise. The percarbonate is most preferably incorporated into such compositions in a coated form which provides in-product stability.

A suitable coating material providing in product stability comprises mixed salt of a water soluble alkali metal sulphate and carbonate. Such coatings together with coating processes have previously been described in GB-1,466,799, granted to Interrox on 9th March 1977. The weight ratio of the mixed salt coating material to percarbonate lies in the range from 1 : 200 to 1 : 4, more preferably from 1 : 99 to 1 : 9, and most preferably from 1 : 49 to 1 : 19. Preferably, the mixed salt is of sodium sulphate and sodium carbonate which has the general formula $\text{Na}_2\text{SO}_4\cdot n\cdot\text{Na}_2\text{CO}_3$ wherein n is from 0.1 to 3, preferably n is from 0.3 to 1.0 and most preferably n is from 0.2 to 0.5.

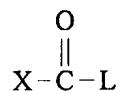
Another suitable coating material providing in product stability, comprises sodium silicate of $\text{SiO}_2 : \text{Na}_2\text{O}$ ratio from 1.8 : 1 to 3.0 : 1, preferably 1.8:1 to 2.4:1, and/or sodium metasilicate, preferably applied at a level of from 2% to 10%, (normally from 3% to 5%) of SiO_2 by weight of the inorganic perhydrate salt. Magnesium silicate can also be included in the coating. Coatings that contain silicate and borate salts or boric acids or other inorganics are also suitable.

Other coatings which contain waxes, oils, fatty soaps can also be used advantageously within the present invention.

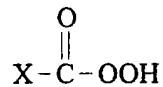
Potassium peroxymonopersulfate is another inorganic perhydrate salt of utility in the compositions herein.

Peroxyacid bleach precursor

Peroxyacid bleach precursors are compounds which react with hydrogen peroxide in a perhydrolysis reaction to produce a peroxyacid. Generally peroxyacid bleach precursors may be represented as



where L is a leaving group and X is essentially any functionality, such that on perhydrolysis the structure of the peroxyacid produced is



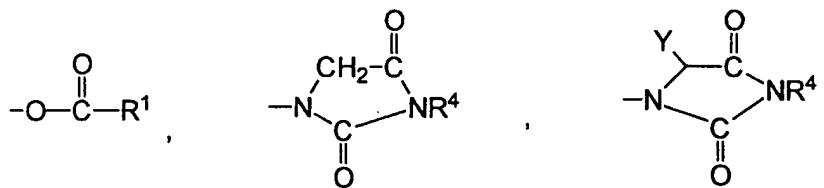
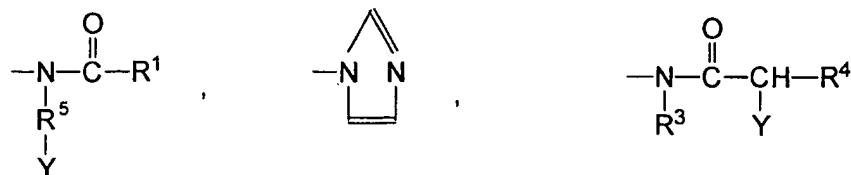
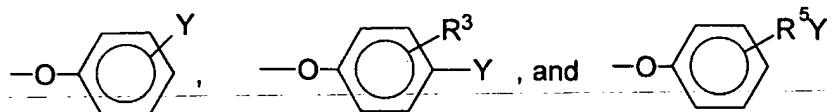
Peroxyacid bleach precursor compounds are preferably incorporated at a level of from 0.5% to 20% by weight, more preferably from 1% to 10% by weight, most preferably from 1.5% to 5% by weight of the compositions.

Suitable peroxyacid bleach precursor compounds typically contain one or more N- or O-acyl groups, which precursors can be selected from a wide range of classes. Suitable classes include anhydrides, esters, imides, lactams and acylated derivatives of imidazoles and oximes. Examples of useful materials within these classes are disclosed in GB-A-1586789. Suitable esters are disclosed in GB-A-836988, 864798, 1147871, 2143231 and EP-A-0170386.

Leaving groups

The leaving group, hereinafter L group, must be sufficiently reactive for the perhydrolysis reaction to occur within the optimum time frame (e.g., a wash cycle). However, if L is too reactive, this activator will be difficult to stabilise for use in a bleaching composition.

Preferred L groups are selected from the group consisting of:



and mixtures thereof, wherein R^1 is an alkyl, aryl, or alkaryl group containing from 1 to 14 carbon atoms, R^3 is an alkyl chain containing from 1 to 8 carbon atoms, R^4 is H or R^5 , R^5 is an alkenyl chain containing from 1 to 8 carbon atoms and Y is H or a solubilizing group. Any of R^1 , R^3 and R^4 may be substituted by essentially any functional group including, for example alkyl, hydroxy, alkoxy, halogen, amine, nitrosyl, amide and ammonium or alkyl ammonium groups.

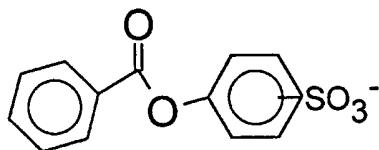
The preferred solubilizing groups are $-\text{SO}_3^-\text{M}^+$, $-\text{CO}_2^-\text{M}^+$, $-\text{SO}_4^-\text{M}^+$, $-\text{N}^+(\text{R}^3)_4\text{X}^-$ and $\text{O}^-\text{N}(\text{R}^3)_3$ and most preferably $-\text{SO}_3^-\text{M}^+$ and $-\text{CO}_2^-\text{M}^+$ wherein R^3 is an alkyl chain containing from 1 to 4 carbon atoms, M is a cation which provides solubility to the bleach activator and X is an anion which provides solubility to the bleach

activator. Preferably, M is an alkali metal, ammonium or substituted ammonium cation, with sodium and potassium being most preferred, and X is a halide, hydroxide, methylsulfate or acetate anion.

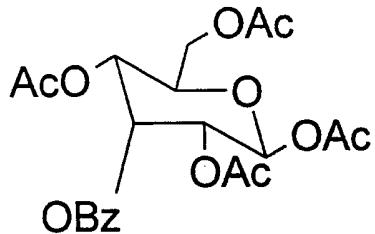
Perbenzoic acid precursor

Perbenzoic acid precursor compounds provide perbenzoic acid on perhydrolysis.

Suitable O-acylated perbenzoic acid precursor compounds include the substituted and unsubstituted benzoyl oxybenzene sulfonates, including for example benzoyl oxybenzene sulfonate:



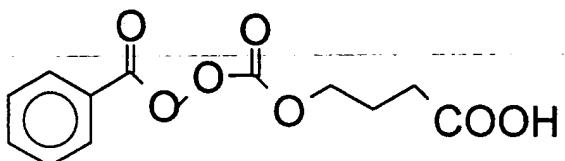
Also suitable are the benzoylation products of sorbitol, glucose, and all saccharides with benzoylating agents, including for example:



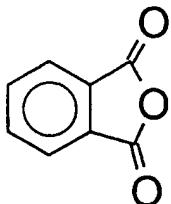
Ac = COCH₃; Bz = Benzoyl

Perbenzoic acid precursor compounds of the imide type include N-benzoyl succinimide, tetrabenzoyl ethylene diamine and the N-benzoyl substituted ureas. Suitable imidazole type perbenzoic acid precursors include N-benzoyl imidazole and N-benzoyl benzimidazole and other useful N-acyl group-containing perbenzoic acid precursors include N-benzoyl pyrrolidone, dibenzoyl taurine and benzoyl pyroglutamic acid.

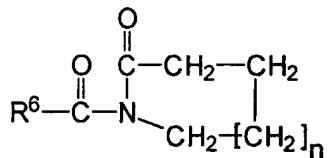
Other perbenzoic acid precursors include the benzoyl diacyl peroxides, the benzoyl tetraacyl peroxides, and the compound having the formula:



Phthalic anhydride is another suitable perbenzoic acid precursor compound herein:



Suitable N-acylated lactam perbenzoic acid precursors have the formula:



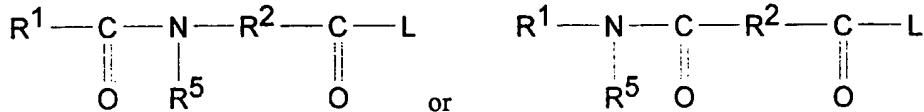
wherein n is from 0 to 8, preferably from 0 to 2, and R⁶ is a benzoyl group.

Perbenzoic acid derivative precursors

Perbenzoic acid derivative precursors provide substituted perbenzoic acids on perhydrolysis.

Suitable substituted perbenzoic acid derivative precursors include any of the herein disclosed perbenzoic precursors in which the benzoyl group is substituted by essentially any non-positively charged (i.e.; non-cationic) functional group including, for example alkyl, hydroxy, alkoxy, halogen, amine, nitrosyl and amide groups.

A preferred class of substituted perbenzoic acid precursor compounds are the amide substituted compounds of the following general formulae:



wherein R^1 is an aryl or alkaryl group with from 1 to 14 carbon atoms, R^2 is an arylene, or alkarylene group containing from 1 to 14 carbon atoms, and R^5 is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms and L can be essentially any leaving group. R^1 preferably contains from 6 to 12 carbon atoms. R^2 preferably contains from 4 to 8 carbon atoms. R^1 may be aryl, substituted aryl or alkylaryl containing branching, substitution, or both and may be sourced from either synthetic sources or natural sources including for example, tallow fat. Analogous structural variations are permissible for R^2 . The substitution can include alkyl, aryl, halogen, nitrogen, sulphur and other typical substituent groups or organic compounds. R^5 is preferably H or methyl. R^1 and R^5 should not contain more than 18 carbon atoms in total. Amide substituted bleach activator compounds of this type are described in EP-A-0170386.

Cationic peroxyacid precursors

Cationic peroxyacid precursor compounds produce cationic peroxyacids on perhydrolysis.

Typically, cationic peroxyacid precursors are formed by substituting the peroxyacid part of a suitable peroxyacid precursor compound with a positively charged functional group, such as an ammonium or alkyl ammonium group, preferably an ethyl or methyl ammonium group. Cationic peroxyacid precursors are typically present in the compositions as a salt with a suitable anion, such as for example a halide ion or a methylsulfate ion.

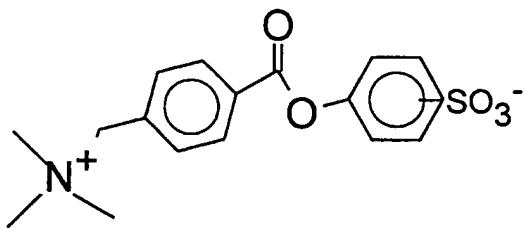
The peroxyacid precursor compound to be so cationically substituted may be a perbenzoic acid, or substituted derivative thereof, precursor compound as described hereinbefore. Alternatively, the peroxyacid precursor compound may be an alkyl percarboxylic acid precursor compound or an amide substituted alkyl peroxyacid

precursor as described hereinafter

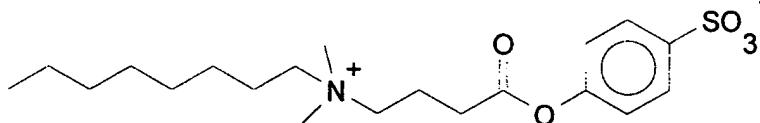
Cationic peroxyacid precursors are described in U.S. Patents 4,904,406; 4,751,015; 4,988,451; 4,397,757; 5,269,962; 5,127,852; 5,093,022; 5,106,528; U.K. 1,382,594; EP 475,512, 458,396 and 284,292; and in JP 87-318,332.

Suitable cationic peroxyacid precursors include any of the ammonium or alkyl ammonium substituted alkyl or benzoyl oxybenzene sulfonates, N-acylated caprolactams, and monobenzoyltetraacetyl glucose benzoyl peroxides.

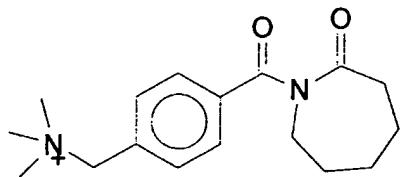
A preferred cationically substituted benzoyl oxybenzene sulfonate is the 4-(trimethyl ammonium) methyl derivative of benzoyl oxybenzene sulfonate:



A preferred cationically substituted alkyl oxybenzene sulfonate has the formula:

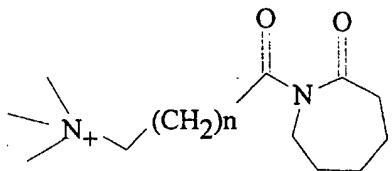


Preferred cationic peroxyacid precursors of the N-acylated caprolactam class include the trialkyl ammonium methylene benzoyl caprolactams, particularly trimethyl ammonium methylene benzoyl caprolactam:



Other preferred cationic peroxyacid precursors of the N-acylated caprolactam class

include the trialkyl ammonium methylene alkyl caprolactams:



where n is from 0 to 12, particularly from 1 to 5.

Another preferred cationic peroxyacid precursor is 2-(N,N,N-trimethyl ammonium) ethyl sodium 4-sulphophenyl carbonate chloride.

Alkyl percarboxylic acid bleach precursors

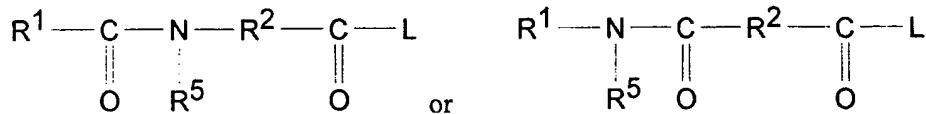
Alkyl percarboxylic acid bleach precursors form percarboxylic acids on perhydrolysis. Preferred precursors of this type provide peracetic acid on perhydrolysis.

Preferred alkyl percarboxylic precursor compounds of the imide type include the N,N,N¹N¹ tetra acetylated alkylene diamines wherein the alkylene group contains from 1 to 6 carbon atoms, particularly those compounds in which the alkylene group contains 1, 2 and 6 carbon atoms. Tetraacetyl ethylene diamine (TAED) is particularly preferred.

Other preferred alkyl percarboxylic acid precursors include sodium 3,5,5-tri-methyl hexanoyloxybenzene sulfonate (iso-NOBS), sodium nonanoyloxybenzene sulfonate (NOBS), sodium acetoxybenzene sulfonate (ABS) and penta acetyl glucose.

Amide substituted alkyl peroxyacid precursors

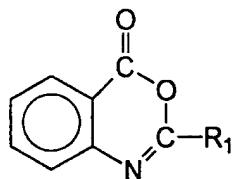
Amide substituted alkyl peroxyacid precursor compounds are also suitable, including those of the following general formulae:



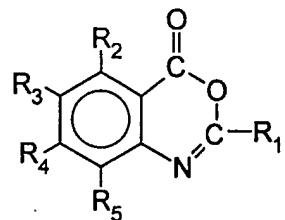
wherein R^1 is an alkyl group with from 1 to 14 carbon atoms, R^2 is an alkylene group containing from 1 to 14 carbon atoms, and R^5 is H or an alkyl group containing 1 to 10 carbon atoms and L can be essentially any leaving group. R^1 preferably contains from 6 to 12 carbon atoms. R^2 preferably contains from 4 to 8 carbon atoms. R^1 may be straight chain or branched alkyl containing branching, substitution, or both and may be sourced from either synthetic sources or natural sources including for example, tallow fat. Analogous structural variations are permissible for R^2 . The substitution can include alkyl, halogen, nitrogen, sulphur and other typical substituent groups or organic compounds. R^5 is preferably H or methyl. R^1 and R^5 should not contain more than 18 carbon atoms in total. Amide substituted bleach activator compounds of this type are described in EP-A-0170386.

Benzoxazin organic peroxyacid precursors

Also suitable are precursor compounds of the benzoxazin-type, as disclosed for example in EP-A-332,294 and EP-A-482,807, particularly those having the formula:

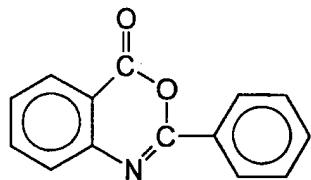


including the substituted benzoxazins of the type



wherein R_1 is H, alkyl, alkaryl, aryl, arylalkyl, and wherein R_2 , R_3 , R_4 , and R_5 may be the same or different substituents selected from H, halogen, alkyl, alkenyl, aryl, hydroxyl, alkoxy, amino, alkyl amino, $COOR_6$ (wherein R_6 is H or an alkyl group) and carbonyl functions.

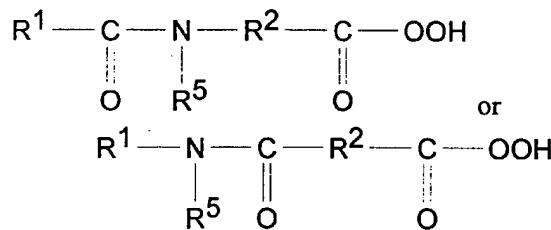
An especially preferred precursor of the benzoxazin-type is:



Preformed organic peroxyacid

The organic peroxyacid bleaching system may contain, in addition to, or as an alternative to, an organic peroxyacid bleach precursor compound, a preformed organic peroxyacid, typically at a level of from 0.5% to 25% by weight, more preferably from 1% to 10% by weight of the composition.

A preferred class of organic peroxyacid compounds are the amide substituted compounds of the following general formulae:



wherein R¹ is an alkyl, aryl or alkaryl group with from 1 to 14 carbon atoms, R² is an alkylene, arylene, and alkarylene group containing from 1 to 14 carbon atoms, and R⁵ is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms. R¹ preferably contains from 6 to 12 carbon atoms. R² preferably contains from 4 to 8 carbon atoms. R¹ may be straight chain or branched alkyl, substituted aryl or alkylaryl containing branching, substitution, or both and may be sourced from either synthetic sources or natural sources including for example, tallow fat. Analogous structural variations are permissible for R². The substitution can include alkyl, aryl, halogen, nitrogen, sulphur and other typical substituent groups or organic compounds. R⁵ is preferably H or methyl. R¹ and R⁵ should not contain more than 18 carbon atoms in total. Amide substituted organic peroxyacid compounds of this type are described in EP-A-0170386.

Other organic peroxyacids include diacyl and tetraacylperoxides, especially diperoxydodecanedioic acid, diperoxytetradecanedioic acid, and diperoxyhexadecanedioic acid. Dibenzoyl peroxide is a preferred organic peroxyacid herein. Mono- and diperazelaic acid, mono- and diperbrassylic acid, and N-phthaloylaminoperoxicaproic acid are also suitable herein.

Controlled rate of release - means

A means may be provided for controlling the rate of release of bleaching agent, particularly oxygen bleach to the wash solution.

Means for controlling the rate of release of the bleach may provide for controlled release of peroxide species to the wash solution. Such means could, for example, include controlling the release of any inorganic perhydrate salt, acting as a hydrogen peroxide source, to the wash solution.

Suitable controlled release means can include confining the bleach to either the compressed or non-compressed portions. Where more than one non-compressed portions are present, the bleach may be confined to the first and/or second and/or optional subsequent non-compressed portions.

Another mechanism for controlling the rate of release of bleach may be by coating the bleach with a coating designed to provide the controlled release. The coating may therefore, for example, comprise a poorly water soluble material, or be a coating of sufficient thickness that the kinetics of dissolution of the thick coating provide the controlled rate of release.

The coating material may be applied using various methods. Any coating material is typically present at a weight ratio of coating material to bleach of from 1:99 to 1:2, preferably from 1:49 to 1:9.

Suitable coating materials include triglycerides (e.g. partially) hydrogenated vegetable oil, soy bean oil, cotton seed oil) mono or diglycerides, microcrystalline waxes, gelatin, cellulose, fatty acids and any mixtures thereof.

Other suitable coating materials can comprise the alkali and alkaline earth metal

sulphates, silicates and carbonates, including calcium carbonate and silicas.

A preferred coating material, particularly for an inorganic perhydrate salt bleach source, comprises sodium silicate of $\text{SiO}_2 : \text{Na}_2\text{O}$ ratio from 1.8 : 1 to 3.0 : 1, preferably 1.8:1 to 2.4:1, and/or sodium metasilicate, preferably applied at a level of from 2% to 10%, (normally from 3% to 5%) of SiO_2 by weight of the inorganic perhydrate salt. Magnesium silicate can also be included in the coating.

Any inorganic salt coating materials may be combined with organic binder materials to provide composite inorganic salt/organic binder coatings. Suitable binders include the C₁₀-C₂₀ alcohol ethoxylates containing from 5 - 100 moles of ethylene oxide per mole of alcohol and more preferably the C₁₅-C₂₀ primary alcohol ethoxylates containing from 20 - 100 moles of ethylene oxide per mole of alcohol.

Other preferred binders include certain polymeric materials. Polyvinylpyrrolidones with an average molecular weight of from 12,000 to 700,000 and polyethylene glycols (PEG) with an average molecular weight of from 600 to 5×10^6 preferably 1000 to 400,000 most preferably 1000 to 10,000 are examples of such polymeric materials. Copolymers of maleic anhydride with ethylene, methylvinyl ether or methacrylic acid, the maleic anhydride constituting at least 20 mole percent of the polymer are further examples of polymeric materials useful as binder agents. These polymeric materials may be used as such or in combination with solvents such as water, propylene glycol and the above mentioned C₁₀-C₂₀ alcohol ethoxylates containing from 5 - 100 moles of ethylene oxide per mole. Further examples of binders include the C₁₀-C₂₀ mono- and diglycerol ethers and also the C₁₀-C₂₀ fatty acids.

Cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose, and homo- or co-polymeric polycarboxylic acids or their salts are other examples of binders suitable for use herein.

One method for applying the coating material involves agglomeration. Preferred agglomeration processes include the use of any of the organic binder materials described hereinabove. Any conventional agglomerator/mixer may be used including, but not limited to pan, rotary drum and vertical blender types. Molten coating compositions may also be applied either by being poured onto, or spray atomized onto a moving bed of bleaching agent.

Other means of providing the required controlled release include mechanical means for altering the physical characteristics of the bleach to control its solubility and rate of release. Suitable protocols could include compression, mechanical injection, manual injection, and adjustment of the solubility of the bleach compound by selection of particle size of any particulate component.

Whilst the choice of particle size will depend both on the composition of the particulate component, and the desire to meet the desired controlled release kinetics, it is desirable that the particle size should be more than 500 micrometers, preferably having an average particle diameter of from 800 to 1200 micrometers.

Additional protocols for providing the means of controlled release include the suitable choice of any other components of the detergent composition matrix such that when the composition is introduced to the wash solution the ionic strength environment therein provided enables the required controlled release kinetics to be achieved.

Metal-containing bleach catalyst

The detergent tablets described herein which contain bleach as a detergent component may additionally contain as a preferred component, a metal containing bleach catalyst. Preferably the metal containing bleach catalyst is a transition metal containing bleach catalyst, more preferably a manganese or cobalt-containing bleach catalyst.

A suitable type of bleach catalyst is a catalyst comprising a heavy metal cation of defined bleach catalytic activity, such as copper, iron cations, an auxiliary metal cation having little or no bleach catalytic activity, such as zinc or aluminium cations, and a sequestrant having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra(methylenephosphonic acid) and water-soluble salts thereof. Such catalysts are disclosed in U.S. Pat. 4,430,243.

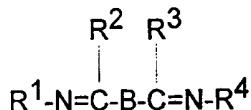
Preferred types of bleach catalysts include the manganese-based complexes disclosed in U.S. Pat. 5,246,621 and U.S. Pat. 5,244,594. Preferred examples of these catalysts include $Mn^{IV}2(u-O)_3(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2\cdot(PF_6)_2$,

$Mn^{III}2(u-O)_1(u-OAc)_2(1,4,7-trimethyl-1,4,7-triazacyclononane)_2-(ClO_4)_2$, $Mn^{IV}4(u-O)_6(1,4,7-triazacyclononane)_4-(ClO_4)_2$, $Mn^{III}Mn^{IV}4(u-O)_1(u-OAc)_2(1,4,7-trimethyl-1,4,7-triazacyclononane)_2-(ClO_4)_3$, and mixtures thereof. Others are described in European patent application publication no. 549,272. Other ligands suitable for use herein include 1,5,9-trimethyl-1,5,9-triazacyclododecane, 2-methyl-1,4,7-triazacyclononane, 2-methyl-1,4,7-triazacyclononane, 1,2,4,7-tetramethyl-1,4,7-triazacyclononane, and mixtures thereof.

The bleach catalysts useful in the compositions herein may also be selected as appropriate for the present invention. For examples of suitable bleach catalysts see U.S. Pat. 4,246,612 and U.S. Pat. 5,227,084. See also U.S. Pat. 5,194,416 which teaches mononuclear manganese (IV) complexes such as $Mn(1,4,7-trimethyl-1,4,7-triazacyclononane)(OCH_3)_3-(PF_6)$.

Still another type of bleach catalyst, as disclosed in U.S. Pat. 5,114,606, is a water-soluble complex of manganese (III), and/or (IV) with a ligand which is a non-carboxylate polyhydroxy compound having at least three consecutive C-OH groups. Preferred ligands include sorbitol, iditol, dulcitol, mannitol, xylitol, arabitol, adonitol, meso-erythritol, meso-inositol, lactose, and mixtures thereof.

U.S. Pat. 5,114,611 teaches a bleach catalyst comprising a complex of transition metals, including Mn, Co, Fe, or Cu, with a non-(macro)-cyclic ligand. Said ligands are of the formula:



wherein R^1 , R^2 , R^3 , and R^4 can each be selected from H, substituted alkyl and aryl groups such that each $R^1-N=C-R^2$ and $R^3-C=N-R^4$ form a five or six-membered ring. Said ring can further be substituted. B is a bridging group selected from O, S, CR⁵R⁶, NR⁷ and C=O, wherein R⁵, R⁶, and R⁷ can each be H, alkyl, or aryl groups, including substituted or unsubstituted groups. Preferred ligands include pyridine, pyridazine, pyrimidine, pyrazine, imidazole, pyrazole, and triazole rings. Optionally, said rings may be substituted with substituents such as alkyl, aryl, alkoxy, halide, and nitro. Particularly preferred is the ligand 2,2'-bispyridylamine. Preferred bleach catalysts include Co, Cu, Mn, Fe, -bispyridylmethane and -bispyridylamine complexes.

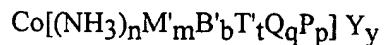
Highly preferred catalysts include $\text{Co}(2,2'\text{-bipyridylamine})\text{Cl}_2$, Di(isothiocyanato)bipyridylamine-cobalt (II), trisdipyridylamine-cobalt(II) perchlorate, $\text{Co}(2,2'\text{-bipyridylamine})_2\text{O}_2\text{ClO}_4$, Bis-(2,2'-bipyridylamine) copper(II) perchlorate, tris(di-2-pyridylamine) iron(II) perchlorate, and mixtures thereof.

Preferred examples include binuclear Mn complexes with tetra-N-dentate and bi-N-dentate ligands, including $\text{N}_4\text{Mn}^{\text{III}}(\text{u-O})_2\text{Mn}^{\text{IV}}\text{N}_4^+$ and $[\text{Bipy}_2\text{Mn}^{\text{III}}(\text{u-O})_2\text{Mn}^{\text{IV}}\text{bipy}_2](\text{ClO}_4)_3$.

While the structures of the bleach-catalyzing manganese complexes of the present invention have not been elucidated, it may be speculated that they comprise chelates or other hydrated coordination complexes which result from the interaction of the carboxyl and nitrogen atoms of the ligand with the manganese cation. Likewise, the oxidation state of the manganese cation during the catalytic process is not known with certainty, and may be the (+II), (+III), (+IV) or (+V) valence state. Due to the ligands' possible six points of attachment to the manganese cation, it may be reasonably speculated that multi-nuclear species and/or "cage" structures may exist in the aqueous bleaching media. Whatever the form of the active Mn-ligand species which actually exists, it functions in an apparently catalytic manner to provide improved bleaching performances on stubborn stains such as tea, ketchup, coffee, wine, juice, and the like.

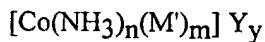
Other bleach catalysts are described, for example, in European patent application, publication no. 408,131 (cobalt complex catalysts), European patent applications, publication nos. 384,503, and 306,089 (metallo-porphyrin catalysts), U.S. 4,728,455 (manganese/multidentate ligand catalyst), U.S. 4,711,748 and European patent application, publication no. 224,952, (absorbed manganese on aluminosilicate catalyst), U.S. 4,601,845 (aluminosilicate support with manganese and zinc or magnesium salt), U.S. 4,626,373 (manganese/ligand catalyst), U.S. 4,119,557 (ferric complex catalyst), German Pat. specification 2,054,019 (cobalt chelant catalyst) Canadian 866,191 (transition metal-containing salts), U.S. 4,430,243 (chelants with manganese cations and non-catalytic metal cations), and U.S. 4,728,455 (manganese gluconate catalysts).

Other preferred examples include cobalt (III) catalysts having the formula:



wherein cobalt is in the +3 oxidation state; n is an integer from 0 to 5 (preferably 4 or 5; most preferably 5); M' represents a monodentate ligand; m is an integer from 0 to 5 (preferably 1 or 2; most preferably 1); B' represents a bidentate ligand; b is an integer from 0 to 2; T' represents a tridentate ligand; t is 0 or 1; Q is a tetradeятate ligand; q is 0 or 1; P is a pentadentate ligand; p is 0 or 1; and $n + m + 2b + 3t + 4q + 5p = 6$; Y is one or more appropriately selected counteranions present in a number y, where y is an integer from 1 to 3 (preferably 2 to 3; most preferably 2 when Y is a -1 charged anion), to obtain a charge-balanced salt, preferred Y are selected from the group consisting of chloride, nitrate, nitrite, sulfate, citrate, acetate, carbonate, and combinations thereof; and wherein further at least one of the coordination sites attached to the cobalt is labile under automatic dishwashing use conditions and the remaining co-ordination sites stabilise the cobalt under automatic dishwashing conditions such that the reduction potential for cobalt (III) to cobalt (II) under alkaline conditions is less than 0.4 volts (preferably less than 0.2 volts) versus a normal hydrogen electrode.

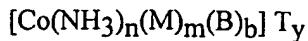
Preferred cobalt catalysts of this type have the formula:



wherein n is an integer from 3 to 5 (preferably 4 or 5; most preferably 5); M' is a labile coordinating moiety, preferably selected from the group consisting of chlorine, bromine, hydroxide, water, and (when m is greater than 1) combinations thereof; m is an integer from 1 to 3 (preferably 1 or 2; most preferably 1); $m+n = 6$; and Y is an appropriately selected counteranion present in a number y, which is an integer from 1 to 3 (preferably 2 to 3; most preferably 2 when Y is a -1 charged anion), to obtain a charge-balanced salt.

The preferred cobalt catalyst of this type useful herein are cobalt pentaamine chloride salts having the formula $[\text{Co}(\text{NH}_3)_5\text{Cl}] \text{Y}_y$, and especially $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$.

More preferred are the present invention compositions which utilize cobalt (III) bleach catalysts having the formula:



wherein cobalt is in the +3 oxidation state; n is 4 or 5 (preferably 5); M is one or more ligands coordinated to the cobalt by one site; m is 0, 1 or 2 (preferably 1); B is a ligand co-ordinated to the cobalt by two sites; b is 0 or 1 (preferably 0), and when b=0, then m+n = 6, and when b=1, then m=0 and n=4; and T is one or more appropriately selected counteranions present in a number y, where y is an integer to obtain a charge-balanced salt (preferably y is 1 to 3; most preferably 2 when T is a -1 charged anion); and wherein further said catalyst has a base hydrolysis rate constant of less than $0.23 \text{ M}^{-1} \text{ s}^{-1}$ (25°C).

Preferred T are selected from the group consisting of chloride, iodide, I_3^- , formate, nitrate, nitrite, sulfate, sulfite, citrate, acetate, carbonate, bromide, PF_6^- , BF_4^- , $\text{B}(\text{Ph})_4^-$, phosphate, phosphite, silicate, tosylate, methanesulfonate, and combinations thereof. Optionally, T can be protonated if more than one anionic group exists in T, e.g., HPO_4^{2-} , HCO_3^- , H_2PO_4^- , etc. Further, T may be selected from the group consisting of non-traditional inorganic anions such as anionic surfactants (e.g., linear alkylbenzene sulfonates (LAS), alkyl sulfates (AS), alkylethoxysulfonates (AES), etc.) and/or anionic polymers (e.g., polyacrylates, polymethacrylates, etc.).

The M moieties include, but are not limited to, for example, F^- , SO_4^{2-} , NCS^- , SCN^- , $\text{S}_2\text{O}_3^{2-}$, NH_3 , PO_4^{3-} , and carboxylates (which preferably are mono-carboxylates, but more than one carboxylate may be present in the moiety as long as the binding to the cobalt is by only one carboxylate per moiety, in which case the other carboxylate in the M moiety may be protonated or in its salt form). Optionally, M can be protonated if more than one anionic group exists in M (e.g., HPO_4^{2-} , HCO_3^- , H_2PO_4^- , $\text{HOC}(\text{O})\text{CH}_2\text{C}(\text{O})\text{O}^-$, etc.) Preferred M moieties are substituted and unsubstituted C₁-C₃₀ carboxylic acids having the formulas:



wherein R is preferably selected from the group consisting of hydrogen and C₁-C₃₀ (preferably C₁-C₁₈) unsubstituted and substituted alkyl, C₆-C₃₀ (preferably C₆-C₁₈) unsubstituted and substituted aryl, and C₃-C₃₀ (preferably C₅-C₁₈) unsubstituted and substituted heteroaryl, wherein substituents are selected from the group consisting of -NR'3, -NR'4⁺, -C(O)OR', -OR', -C(O)NR'2, wherein R' is selected from the group

consisting of hydrogen and C₁-C₆ moieties. Such substituted R therefore include the moieties -(CH₂)_nOH and -(CH₂)_nNR'4⁺, wherein n is an integer from 1 to 16, preferably from 2 to 10, and most preferably from 2 to 5.

Most preferred M are carboxylic acids having the formula above wherein R is selected from the group consisting of hydrogen, methyl, ethyl, propyl, straight or branched C₄-C₁₂ alkyl, and benzyl. Most preferred R is methyl. Preferred carboxylic acid M moieties include formic, benzoic, octanoic, nonanoic, decanoic, dodecanoic, malonic, maleic, succinic, adipic, phthalic, 2-ethylhexanoic, naphthenoic, oleic, palmitic, triflate, tartrate, stearic, butyric, citric, acrylic, aspartic, fumaric, lauric, linoleic, lactic, malic, and especially acetic acid.

The B moieties include carbonate, di- and higher carboxylates (e.g., oxalate, malonate, malic, succinate, maleate), picolinic acid, and alpha and beta amino acids (e.g., glycine, alanine, beta-alanine, phenylalanine).

Cobalt bleach catalysts useful herein are known, being described for example along with their base hydrolysis rates, in M. L. Tobe, "Base Hydrolysis of Transition-Metal Complexes", Adv. Inorg. Bioinorg. Mech., (1983), 2, pages 1-94. For example, Table 1 at page 17, provides the base hydrolysis rates (designated therein as k_{OH}) for cobalt pentaamine catalysts complexed with oxalate (k_{OH}= 2.5 x 10⁻⁴ M⁻¹ s⁻¹ (25° C)), NCS⁻ (k_{OH}= 5.0 x 10⁻⁴ M⁻¹ s⁻¹ (25°C)), formate (k_{OH}= 5.8 x 10⁻⁴ M⁻¹ s⁻¹ (25°C)), and acetate (k_{OH}= 9.6 x 10⁻⁴ M⁻¹ s⁻¹ (25°C)). The most preferred cobalt catalyst useful herein are cobalt pentaamine acetate salts having the formula [Co(NH₃)₅OAc]_{T_y}, wherein OAc represents an acetate moiety, and especially cobalt pentaamine acetate chloride, [Co(NH₃)₅OAc]Cl₂; as well as [Co(NH₃)₅OAc](OAc)₂; [Co(NH₃)₅OAc](PF₆)₂; [Co(NH₃)₅OAc](SO₄); [Co(NH₃)₅OAc](BF₄)₂; and [Co(NH₃)₅OAc](NO₃)₂ (herein "PAC").

These cobalt catalysts are readily prepared by known procedures, such as taught for example in the Tobe article hereinbefore and the references cited therein, in U.S. Patent 4,810,410, to Diakun et al, issued March 7, 1989, J. Chem. Ed. (1989), 66 (12), 1043-45; The Synthesis and Characterization of Inorganic Compounds, W.L. Jolly (Prentice-Hall; 1970), pp. 461-3; Inorg. Chem., 18, 1497-1502 (1979); Inorg. Chem., 21, 2881-2885 (1982); Inorg. Chem., 18, 2023-2025 (1979); Inorg. Synthesis, 173-176 (1960); and Journal of Physical Chemistry, 56, 22-25 (1952); as

well as the synthesis examples provided hereinafter.

Cobalt catalysts suitable for incorporation into the detergent tablets of the present invention may be produced according to the synthetic routes disclosed in U.S. Patent Nos. 5,559,261, 5,581,005, and 5,597,936, the disclosures of which are herein incorporated by reference.

These catalysts may be co-processed with adjunct materials so as to reduce the colour impact if desired for the aesthetics of the product, or to be included in enzyme-containing particles as exemplified hereinafter, or the compositions may be manufactured to contain catalyst "speckles".

Organic polymeric compound

Organic polymeric compounds may be added as preferred components of the detergent tablets in accord with the invention. By organic polymeric compound it is meant essentially any polymeric organic compound commonly found in detergent compositions having dispersant, anti-redeposition, soil release agents or other detygency properties.

Organic polymeric compound is typically incorporated in the detergent compositions of the invention at a level of from 0.1% to 30%, preferably from 0.5% to 15%, most preferably from 1% to 10% by weight of the compositions.

Examples of organic polymeric compounds include the water soluble organic homo- or co-polymeric polycarboxylic acids, modified polycarboxylates or their salts in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of the latter type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of molecular weight 2000-10000 and their copolymers with any suitable other monomer units including modified acrylic, fumaric, maleic, itaconic, aconitic, mesaconic, citraconic and methylenemalonic acid or their salts, maleic anhydride, acrylamide, alkylene, vinylmethyl ether, styrene and any mixtures thereof. Preferred are the copolymers of acrylic acid and maleic anhydride having a molecular weight of from 20,000 to 100,000.

Preferred commercially available acrylic acid containing polymers having a molecular weight below 15,000 include those sold under the tradename Sokalan PA30, PA20, PA15, PA10 and Sokalan CP10 by BASF GmbH, and those sold under the tradename Acusol 45N, 480N, 460N by Rohm and Haas.

Preferred acrylic acid containing copolymers include those which contain as monomer units: a) from 90% to 10%, preferably from 80% to 20% by weight acrylic acid or its salts and b) from 10% to 90%, preferably from 20% to 80% by weight of a substituted acrylic monomer or its salts having the general formula -[CR₂-CR₁(CO-O-R₃)]- wherein at least one of the substituents R₁, R₂ or R₃, preferably R₁ or R₂ is a 1 to 4 carbon alkyl or hydroxyalkyl group, R₁ or R₂ can be a hydrogen and R₃ can be a hydrogen or alkali metal salt. Most preferred is a substituted acrylic monomer wherein R₁ is methyl, R₂ is hydrogen (i.e. a methacrylic acid monomer). The most preferred copolymer of this type has a molecular weight of 3500 and contains 60% to 80% by weight of acrylic acid and 40% to 20% by weight of methacrylic acid.

The polyamine and modified polyamine compounds are useful herein including those derived from aspartic acid such as those disclosed in EP-A-305282, EP-A-305283 and EP-A-351629.

Other optional polymers may polyvinyl alcohols and acetates both modified and non-modified, cellulosics and modified cellulosics, polyoxyethylenes, polyoxypropylenes, and copolymers thereof, both modified and non-modified, terephthalate esters of ethylene or propylene glycol or mixtures thereof with polyoxyalkylene units.

Suitable examples are disclosed in US patent Nos. 5,591,703, 5,597,789 and 4,490,271.

Soil Release Agents

Suitable polymeric soil release agents include those soil release agents having: (a) one or more nonionic hydrophile components consisting essentially of (i) polyoxyethylene segments with a degree of polymerization of at least 2, or (ii) oxypropylene or polyoxypropylene segments with a degree of polymerization of from 2 to 10, wherein said hydrophile segment does not encompass any oxypropylene unit unless it is bonded to adjacent moieties at each end by ether linkages, or (iii) a mixture of

oxyalkylene units comprising oxyethylene and from 1 to 30 oxypropylene units, said hydrophile segments preferably comprising at least 25% oxyethylene units and more preferably, especially for such components having 20 to 30 oxypropylene units, at least 50% oxyethylene units; or (b) one or more hydrophobe components comprising (i) C₃ oxyalkylene terephthalate segments, wherein, if said hydrophobe components also comprise oxyethylene terephthalate, the ratio of oxyethylene terephthalate:C₃ oxyalkylene terephthalate units is 2:1 or lower, (ii) C₄-C₆ alkylene or oxy C₄-C₆ alkylene segments, or mixtures therein, (iii) poly (vinyl ester) segments, preferably polyvinyl acetate, having a degree of polymerization of at least 2, or (iv) C₁-C₄ alkyl ether or C₄ hydroxyalkyl ether substituents, or mixtures therein, wherein said substituents are present in the form of C₁-C₄ alkyl ether or C₄ hydroxyalkyl ether cellulose derivatives, or mixtures therein, or a combination of (a) and (b).

Typically, the polyoxyethylene segments of (a)(i) will have a degree of polymerization of from 200, although higher levels can be used, preferably from 3 to 150, more preferably from 6 to 100. Suitable oxy C₄-C₆ alkylene hydrophobe segments include, but are not limited to, end-caps of polymeric soil release agents such as MO₃S(CH₂)_nOCH₂CH₂O-, where M is sodium and n is an integer from 4-6, as disclosed in U.S. Patent 4,721,580, issued January 26, 1988 to Gosselink.

Polymeric soil release agents useful herein also include cellulosic derivatives such as hydroxyether cellulosic polymers, copolymeric blocks of ethylene terephthalate or propylene terephthalate with polyethylene oxide or polypropylene oxide terephthalate, and the like. Such agents are commercially available and include hydroxyethers of cellulose such as METHOCEL (Dow). Cellulosic soil release agents for use herein also include those selected from the group consisting of C₁-C₄ alkyl and C₄ hydroxyalkyl cellulose; see U.S. Patent 4,000,093, issued December 28, 1976 to Nicol, et al.

Soil release agents characterized by poly(vinyl ester) hydrophobe segments include graft copolymers of poly(vinyl ester), e.g., C₁-C₆ vinyl esters, preferably poly(vinyl acetate) grafted onto polyalkylene oxide backbones, such as polyethylene oxide backbones. See European Patent Application 0 219 048, published April 22, 1987 by Kud, et al.

Another suitable soil release agent is a copolymer having random blocks of ethylene

terephthalate and polyethylene oxide (PEO) terephthalate. The molecular weight of this polymeric soil release agent is in the range of from 25,000 to 55,000. See U.S. Patent 3,959,230 to Hays, issued May 25, 1976 and U.S. Patent 3,893,929 to Basadur issued July 8, 1975.

Another suitable polymeric soil release agent is a polyester with repeat units of ethylene terephthalate units contains 10-15% by weight of ethylene terephthalate units together with 90-80% by weight of polyoxyethylene terephthalate units, derived from a polyoxyethylene glycol of average molecular weight 300-5,000.

Another suitable polymeric soil release agent is a sulfonated product of a substantially linear ester oligomer comprised of an oligomeric ester backbone of terephthaloyl and oxyalkyleneoxy repeat units and terminal moieties covalently attached to the backbone. These soil release agents are described fully in U.S. Patent 4,968,451, issued November 6, 1990 to J.J. Scheibel and E.P. Gosselink. Other suitable polymeric soil release agents include the terephthalate polyesters of U.S. Patent 4,711,730, issued December 8, 1987 to Gosselink et al, the anionic end-capped oligomeric esters of U.S. Patent 4,721,580, issued January 26, 1988 to Gosselink, and the block polyester oligomeric compounds of U.S. Patent 4,702,857, issued October 27, 1987 to Gosselink. Other polymeric soil release agents also include the soil release agents of U.S. Patent 4,877,896, issued October 31, 1989 to Maldonado et al, which discloses anionic, especially sulfoaroyl, end-capped terephthalate esters.

Another soil release agent is an oligomer with repeat units of terephthaloyl units, sulfoisoterephthaloyl units, oxyethyleneoxy and oxy-1,2-propylene units. The repeat units form the backbone of the oligomer and are preferably terminated with modified isethionate end-caps. A particularly preferred soil release agent of this type comprises one sulfoisophthaloyl unit, 5 terephthaloyl units, oxyethyleneoxy and oxy-1,2-propyleneoxy units in a ratio of from 1.7 to 1.8, and two end-cap units of sodium 2-(2-hydroxyethoxy)-ethanesulfonate.

Heavy metal ion sequestrant

The detergent tablets of the invention preferably contain as an optional component a heavy metal ion sequestrant. By heavy metal ion sequestrant it is meant herein components which act to sequester (chelate) heavy metal ions. These components

may also have calcium and magnesium chelation capacity, but preferentially they show selectivity to binding heavy metal ions such as iron, manganese and copper.

Heavy metal ion sequestrants are generally present at a level of from 0.005% to 20%, preferably from 0.1% to 10%, more preferably from 0.25% to 7.5% and most preferably from 0.5% to 5% by weight of the compositions.

Heavy metal ion sequestrants, which are acidic in nature, having for example phosphonic acid or carboxylic acid functionalities, may be present either in their acid form or as a complex/salt with a suitable counter cation such as an alkali or alkaline metal ion, ammonium, or substituted ammonium ion, or any mixtures thereof. Preferably any salts/complexes are water soluble. The molar ratio of said counter cation to the heavy metal ion sequestrant is preferably at least 1:1.

Suitable heavy metal ion sequestrants for use herein include organic phosphonates, such as the amino alkylene poly (alkylene phosphonates), alkali metal ethane 1-hydroxy disphosphonates and nitrilo trimethylene phosphonates. Preferred among the above species are diethylene triamine penta (methylene phosphonate), ethylene diamine tri (methylene phosphonate) hexamethylene diamine tetra (methylene phosphonate) and hydroxy-ethylene 1,1 diphosphonate.

Other suitable heavy metal ion sequestrant for use herein include nitrilotriacetic acid and polyaminocarboxylic acids such as ethylenediaminetetraacetic acid, ethylenetriamine pentacetic acid, ethylenediamine disuccinic acid, ethylenediamine diglutaric acid, 2-hydroxypropylenediamine disuccinic acid or any salts thereof.

Especially preferred is ethylenediamine-N,N'-disuccinic acid (EDDS) or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof. Preferred EDDS compounds are the free acid form and the sodium or magnesium salt or complex thereof.

Crystal growth inhibitor component

The detergent tablets preferably contain a crystal growth inhibitor component, preferably an organodiphosphonic acid component, incorporated preferably at a level of from 0.01% to 5%, more preferably from 0.1% to 2% by weight of the

compositions.

By organo diphosphonic acid it is meant herein an organo diphosphonic acid which does not contain nitrogen as part of its chemical structure. This definition therefore excludes the organo aminophosphonates, which however may be included in compositions of the invention as heavy metal ion sequestrant components.

The organo diphosphonic acid is preferably a C₁-C₄ diphosphonic acid, more preferably a C₂ diphosphonic acid, such as ethylene diphosphonic acid, or most preferably ethane 1-hydroxy-1,1-diphosphonic acid (HEDP) and may be present in partially or fully ionized form, particularly as a salt or complex.

Water-soluble sulfate salt

The detergent tablet optionally contains a water-soluble sulfate salt. Where present the water-soluble sulfate salt is at the level of from 0.1% to 40%, more preferably from 1% to 30%, most preferably from 5% to 25% by weight of the compositions.

The water-soluble sulfate salt may be essentially any salt of sulfate with any counter cation. Preferred salts are selected from the sulfates of the alkali and alkaline earth metals, particularly sodium sulfate.

Alkali Metal Silicate

The detergent tablets of the present invention preferably an alkali meta. A preferred alkali metal silicate is sodium silicate having an SiO₂:Na₂O ratio of from 1.8 to 3.0, preferably from 1.8 to 2.4, most preferably 2.0. Sodium silicate is preferably present at a level of less than 20%, preferably from 1% to 15%, most preferably from 3% to 12% by weight of SiO₂. The alkali metal silicate may be in the form of either the anhydrous salt or a hydrated salt.

Alkali metal silicate may also be present as a component of an alkalinity system.

The alkalinity system also preferably contains sodium metasilicate, present at a level of at least 0.4% SiO₂ by weight. Sodium metasilicate has a nominal SiO₂ : Na₂O ratio of 1.0. The weight ratio of said sodium silicate to said sodium metasilicate,

measured as SiO₂, is preferably from 50:1 to 5:4, more preferably from 15:1 to 2:1, most preferably from 10:1 to 5:2.

Colourant

The term 'colourant', as used herein, means any substance that absorbs specific wavelengths of light from the visible light spectrum. Such colourants when added to a detergent composition have the effect of changing the visible colour and thus the appearance of the detergent composition. Colourants may be for example either dyes or pigments. Preferably the colourants are stable in composition in which they are to be incorporated. Thus in a composition of high pH the colourant is preferably alkali stable and in a composition of low pH the colourant is preferably acid stable.

The compressed portion and/or non compressed may contain a colourant, a mixture of colourants, coloured particles or mixture of coloured particles such that the compressed portion and the non-compressed portion have different visual appearances. Preferably one of either the compressed portion or the non-compressed comprises a colourant.

Where the non-compressed portion comprises two or more compositions of active detergent components, preferably at least one of either the first and second and/or subsequent compositions comprises a colourant. Where both the first and second and/or subsequent compositions comprise a colourant it is preferred that the colourants have a different visual appearance.

Where present the coating layer preferably comprises a colourant. Where the compressed portion and the coating layer comprise a colourant, it is preferred that the colourants provide a different visual effect.

Examples of suitable dyes include reactive dyes, direct dyes, azo dyes. Preferred dyes include phthalocyanine dyes, anthraquinone dye, quinoline dyes, monoazo, disazo and polyazo. More preferred dyes include anthraquinone, quinoline and monoazo dyes. Preferred dyes include SANDOLAN E-HRL 180% (tradename), SANDOLAN MILLING BLUE (tradename), TURQUOISE ACID BLUE (tradename) and SANDOLAN BRILLIANT GREEN (tradename) all available from Clariant UK, HEXACOL QUINOLINE YELLOW (tradename) and HEXACOL BRILLIANT

BLUE (tradename) both available from Pointings, UK, ULTRA MARINE BLUE (tradename) available from Holliday or LEVAFIX TURQUISE BLUE EBA (tradename) available from Bayer, USA.

The colourant may be incorporated into the compressed and/or non-compressed portion by any suitable method. Suitable methods include mixing all or selected active detergent components with a colourant in a drum or spraying all or selected active detergent components with the colourant in a rotating drum.

Colourant when present as a component of the compressed portion is present at a level of from 0.001% to 1.5%, preferably from 0.01% to 1.0%, most preferably from 0.1% to 0.3%. When present as a component of the non-compressed portion, colourant is generally present at a level of from 0.001% to 0.1%, more preferably from 0.005% to 0.05%, most preferably from 0.007% to 0.02%. When present as a component of the coating layer, colourant is present at a level of from 0.01% to 0.5%, more preferably from 0.02% to 0.1%, most preferably from 0.03% to 0.06%.

Corrosion inhibitor compound

The detergent tablets of the present invention suitable for use in dishwashing methods may contain corrosion inhibitors preferably selected from organic silver coating agents, particularly paraffin, nitrogen-containing corrosion inhibitor compounds and Mn(II) compounds, particularly Mn(II) salts of organic ligands.

Organic silver coating agents are described in PCT Publication No. WO94/16047 and copending European application No. EP-A-690122. Nitrogen-containing corrosion inhibitor compounds are disclosed in copending European Application no. EP-A-634,478. Mn(II) compounds for use in corrosion inhibition are described in copending European Application No. EP-A-672 749.

Organic silver coating agent may be incorporated at a level of from 0.05% to 10%, preferably from 0.1% to 5% by weight of the total composition.

The functional role of the silver coating agent is to form 'in use' a protective coating layer on any silverware components of the washload to which the compositions of the invention are being applied. The silver coating agent should hence have a high affinity

for attachment to solid silver surfaces, particularly when present in as a component of an aqueous washing and bleaching solution with which the solid silver surfaces are being treated.

Suitable organic silver coating agents herein include fatty esters of mono- or polyhydric alcohols having from 1 to 40 carbon atoms in the hydrocarbon chain.

The fatty acid portion of the fatty ester can be obtained from mono- or polycarboxylic acids having from 1 to 40 carbon atoms in the hydrocarbon chain.

Suitable examples of monocarboxylic fatty acids include behenic acid, stearic acid, oleic acid, palmitic acid, myristic acid, lauric acid, acetic acid, propionic acid, butyric acid, isobutyric acid, Valerie acid, lactic acid, glycolic acid and β, β' -dihydroxyisobutyric acid. Examples of suitable polycarboxylic acids include: n-butylmalonic acid, isocitric acid, citric acid, maleic acid, malic acid and succinic acid.

The fatty alcohol radical in the fatty ester can be represented by mono- or polyhydric alcohols having from 1 to 40 carbon atoms in the hydrocarbon chain. Examples of suitable fatty alcohols include; behenyl, arachidyl, cocoyl, oleyl and lauryl alcohol, ethylene glycol, glycerol, ethanol, isopropanol, vinyl alcohol, diglycerol, xylitol, sucrose, erythritol, pentaerythritol, sorbitol or sorbitan.

Preferably, the fatty acid and/or fatty alcohol group of the fatty ester adjunct material have from 1 to 24 carbon atoms in the alkyl chain.

Preferred fatty esters herein are ethylene glycol, glycerol and sorbitan esters wherein the fatty acid portion of the ester normally comprises a species selected from behenic acid, stearic acid, oleic acid, palmitic acid or myristic acid.

The glycerol esters are also highly preferred. These are the mono-, di- or tri-esters of glycerol and the fatty acids as defined above.

Specific examples of fatty alcohol esters for use herein include: stearyl acetate, palmityl di-lactate, cocoyl isobutyrate, oleyl maleate, oleyl dimaleate, and tallowyl propionate. Fatty acid esters useful herein include: xylitol monopalmitate, pentaerythritol monostearate, sucrose monostearate, glycerol monostearate, ethylene glycol monostearate, sorbitan esters. Suitable sorbitan esters include sorbitan

monostearate, sorbitan palmitate, sorbitan monolaurate, sorbitan monomyristate, sorbitan monobehenate, sorbitan mono-oleate, sorbitan dilaurate, sorbitan distearate, sorbitan dibehenate, sorbitan dioleate, and also mixed tallowalkyl sorbitan mono- and di-esters.

Glycerol monostearate, glycerol mono-oleate, glycerol monopalmitate, glycerol monobehenate, and glycerol distearate are preferred glycerol esters herein.

Suitable organic silver coating agents include triglycerides, mono or diglycerides, and wholly or partially hydrogenated derivatives thereof, and any mixtures thereof.

Suitable sources of fatty acid esters include vegetable and fish oils and animal fats.

Suitable vegetable oils include soy bean oil, cotton seed oil, castor oil, olive oil, peanut oil, safflower oil, sunflower oil, rapeseed oil, grapeseed oil, palm oil and corn oil.

Waxes, including microcrystalline waxes are suitable organic silver coating agents herein. Preferred waxes have a melting point in the range from 35°C to 110°C and comprise generally from 12 to 70 carbon atoms. Preferred are petroleum waxes of the paraffin and microcrystalline type which are composed of long-chain saturated hydrocarbon compounds.

Alginates and gelatin are suitable organic silver coating agents herein.

Dialkyl amine oxides such as C₁₂-C₂₀ methylamine oxide, and dialkyl quaternary ammonium compounds and salts, such as the C₁₂-C₂₀ methylammonium halides are also suitable.

Other suitable organic silver coating agents include certain polymeric materials. Polyvinylpyrrolidones with an average molecular weight of from 12,000 to 700,000, polyethylene glycols (PEG) with an average molecular weight of from 600 to 10,000, polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, and cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose are examples of such polymeric materials.

Certain perfume materials, particularly those demonstrating a high substantivity for

metallic surfaces, are also useful as the organic silver coating agents herein.

Polymeric soil release agents can also be used as an organic silver coating agent.

A preferred organic silver coating agent is a paraffin oil, typically a predominantly branched aliphatic hydrocarbon having a number of carbon atoms in the range of from 20 to 50; preferred paraffin oil selected from predominantly branched C₂₅₋₄₅ species with a ratio of cyclic to noncyclic hydrocarbons of from 1:10 to 2:1, preferably from 1:5 to 1:1. A paraffin oil meeting these characteristics, having a ratio of cyclic to noncyclic hydrocarbons of 32:68, is sold by Wintershall, Salzbergen, Germany, under the trade name WINOG 70.

Nitrogen-containing corrosion inhibitor compounds

Suitable nitrogen-containing corrosion inhibitor compounds include imidazole and derivatives thereof such as benzimidazole, 2-heptadecyl imidazole and those imidazole derivatives described in Czech Patent No. 139, 279 and British Patent GB-A-1,137,741, which also discloses a method for making imidazole compounds.

Also suitable as nitrogen-containing corrosion inhibitor compounds are pyrazole compounds and their derivatives, particularly those where the pyrazole is substituted in any of the 1, 3, 4 or 5 positions by substituents R₁, R₃, R₄ and R₅ where R₁ is any of H, CH₂OH, CONH₃, or COCH₃, R₃ and R₅ are any of C₁-C₂₀ alkyl or hydroxyl, and R₄ is any of H, NH₂ or NO₂.

Other suitable nitrogen-containing corrosion inhibitor compounds include benzotriazole, 2-mercaptopbenzothiazole, 1-phenyl-5-mercpto-1,2,3,4-tetrazole, thionalide, morpholine, melamine, distearylamine, stearoyl stearamide, cyanuric acid, aminotriazole, aminotetrazole and indazole.

Nitrogen-containing compounds such as amines, especially distearylamine and ammonium compounds such as ammonium chloride, ammonium bromide, ammonium sulphate or diammonium hydrogen citrate are also suitable.

Mn(II) corrosion inhibitor compounds

The detergent tablets may contain an Mn(II) corrosion inhibitor compound. The Mn(II) compound is preferably incorporated at a level of from 0.005% to 5% by weight, more preferably from 0.01% to 1%, most preferably from 0.02% to 0.4% by weight of the compositions. Preferably, the Mn(II) compound is incorporated at a level to provide from 0.1 ppm to 250 ppm, more preferably from 0.5 ppm to 50 ppm, most preferably from 1 ppm to 20 ppm by weight of Mn(II) ions in any bleaching solution.

The Mn (II) compound may be an inorganic salt in anhydrous, or any hydrated forms. Suitable salts include manganese sulphate, manganese carbonate, manganese phosphate, manganese nitrate, manganese acetate and manganese chloride. The Mn(II) compound may be a salt or complex of an organic fatty acid such as manganese acetate or manganese stearate.

The Mn(II) compound may be a salt or complex of an organic ligand. In one preferred aspect the organic ligand is a heavy metal ion sequestrant. In another preferred aspect the organic ligand is a crystal growth inhibitor.

Other corrosion inhibitor compounds

Other suitable additional corrosion inhibitor compounds include, mercaptans and diols, especially mercaptans with 4 to 20 carbon atoms including lauryl mercaptan, thiophenol, thionaphthol, thionalide and thioanthranol. Also suitable are saturated or unsaturated C₁₀-C₂₀ fatty acids, or their salts, especially aluminium tristearate. The C₁₂-C₂₀ hydroxy fatty acids, or their salts, are also suitable. Phosphonated octadecane and other anti-oxidants such as betahydroxytoluene (BHT) are also suitable.

Copolymers of butadiene and maleic acid, particularly those supplied under the trade reference no. 07787 by Polysciences Inc have been found to be of particular utility as corrosion inhibitor compounds.

Hydrocarbon oils

Another preferred detergent component for use in the present invention is a hydrocarbon oil, typically a predominantly long chain, aliphatic hydrocarbons having a number of carbon atoms in the range of from 20 to 50; preferred hydrocarbons are

saturated and/or branched; preferred hydrocarbon oil selected from predominantly branched C₂₅-45 species with a ratio of cyclic to noncyclic hydrocarbons of from 1:10 to 2:1, preferably from 1:5 to 1:1. A preferred hydrocarbon oil is paraffin. A paraffin oil meeting the characteristics as outlined above, having a ratio of cyclic to noncyclic hydrocarbons of 32:68, is sold by Wintershall, Salzbergen, Germany, under the trade name WINOG 70.

Water-soluble bismuth compound

The detergent tablets of the present invention suitable for use in dishwashing methods may contain a water-soluble bismuth compound, preferably present at a level of from 0.005% to 20%, more preferably from 0.01% to 5%, most preferably from 0.1% to 1% by weight of the compositions.

The water-soluble bismuth compound may be essentially any salt or complex of bismuth with essentially any inorganic or organic counter anion. Preferred inorganic bismuth salts are selected from the bismuth trihalides, bismuth nitrate and bismuth phosphate. Bismuth acetate and citrate are preferred salts with an organic counter anion.

Enzyme Stabilizing System

Preferred enzyme-containing compositions herein may comprise from 0.001% to 10%, preferably from 0.005% to 8%, most preferably from 0.01% to 6%, by weight of an enzyme stabilizing system. The enzyme stabilizing system can be any stabilizing system which is compatible with the deteritive enzyme. Such stabilizing systems can comprise calcium ion, boric acid, propylene glycol, short chain carboxylic acid, boronic acid, chlorine bleach scavengers and mixtures thereof. Such stabilizing systems can also comprise reversible enzyme inhibitors, such as reversible protease inhibitors.

Lime soap dispersant compound

The detergent tablets may contain a lime soap dispersant compound, preferably present at a level of from 0.1% to 40% by weight, more preferably 1% to 20% by weight, most preferably from 2% to 10% by weight of the compositions.

A lime soap dispersant is a material that prevents the precipitation of alkali metal, ammonium or amine salts of fatty acids by calcium or magnesium ions. Preferred lime soap disperant compounds are disclosed in PCT Application No. WO93/08877.

Suds suppressing system

The detergent tablets of the present invention, particularly when formulated for use in automatic dishwashers, preferably comprise a suds suppressing system present at a level of from 0.01% to 15%, preferably from 0.05% to 10%, most preferably from 0.1% to 5% by weight of the composition.

Suitable suds suppressing systems for use herein may comprise essentially any known antifoam compound, including, for example silicone antifoam compounds, 2-alkyl and alanol antifoam compounds. Preferred suds suppressing systems and antifoam compounds are disclosed in PCT Application No. WO93/08876 and EP-A-705 324.

Polymeric dye transfer inhibiting agents

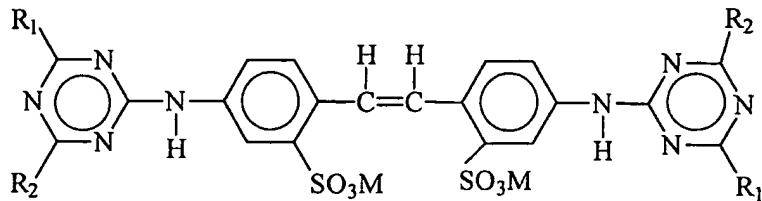
The detergent tablets herein may also comprise from 0.01% to 10 %, preferably from 0.05% to 0.5% by weight of polymeric dye transfer inhibiting agents.

The polymeric dye transfer inhibiting agents are preferably selected from polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidonepolymers or combinations thereof.

Optical brightener

The detergent tablets suitable for use in laundry washing methods as described herein, also optionally contain from 0.005% to 5% by weight of certain types of hydrophilic optical brighteners.

Hydrophilic optical brighteners useful herein include those having the structural formula:



wherein R₁ is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; R₂ is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morphilino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

When in the above formula, R₁ is anilino, R₂ is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the detergent compositions herein.

When in the above formula, R₁ is anilino, R₂ is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation.

When in the above formula, R₁ is anilino, R₂ is morphilino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species is commercially marketed under the tradename Tinopal AMS-GX by Ciba Geigy Corporation.

Clay softening system

The detergent tablets suitable for use in laundry cleaning methods may contain a clay softening system comprising a clay mineral compound and optionally a clay flocculating agent.

The clay mineral compound is preferably a smectite clay compound. Smectite clays are disclosed in the US Patents No.s 3,862,058, 3,948,790, 3,954,632 and 4,062,647. European Patents No.s EP-A-299,575 and EP-A-313,146 in the name of the Procter and Gamble Company describe suitable organic polymeric clay flocculating agents.

Cationic fabric softening agents

Cationic fabric softening agents can also be incorporated into compositions in accordance with the present invention which are suitable for use in methods of laundry washing. Suitable cationic fabric softening agents include the water insoluble tertiary amines or dilong chain amide materials as disclosed in GB-A-1 514 276 and EP-B-0 011 340.

Cationic fabric softening agents are typically incorporated at total levels of from 0.5% to 15% by weight, normally from 1% to 5% by weight.

Other optional ingredients

Other optional components suitable for inclusion in the compositions of the invention include perfumes, especially encapsulated perfumes, pro-perfumes or mixtures thereof as described in the Applicants copending application (attorney docket number CM 1645F) and filler salts, with sodium sulfate being a preferred filler salt.

pH of the compositions

The detergent tablets of the present invention are preferably not formulated to have an unduly high pH, in preference having a pH measured as a 1% solution in distilled water of from 8.0 to 12.5, more preferably from 9.0 to 11.8, most preferably from 9.5 to 11.5.

In another aspect of the present invention the compressed and non-compressed portions are formulated to deliver different pH.

Machine dishwashing method

Any suitable methods for machine washing or cleaning soiled tableware are envisaged.

A preferred machine dishwashing method comprises treating soiled articles selected from crockery, glassware, silverware, metallic items, cutlery and mixtures thereof, with an aqueous liquid having dissolved or dispersed therein an effective amount of a detergent tablet in accord with the invention. By an effective amount of the detergent tablet it is meant from 8g to 60g of product dissolved or dispersed in a wash solution of volume from 3 to 10 litres, as are typical product dosages and wash solution volumes commonly employed in conventional machine dishwashing methods. Preferably the detergent tablets are from 15g to 40g in weight, more preferably from 20g to 35g in weight.

Laundry washing method

Machine laundry methods herein typically comprise treating soiled laundry with an aqueous wash solution in a washing machine having dissolved or dispersed therein an effective amount of a machine laundry detergent tablet composition in accord with the invention. By an effective amount of the detergent tablet composition it is meant from 40g to 300g of product dissolved or dispersed in a wash solution of volume from 5 to 65 litres, as are typical product dosages and wash solution volumes commonly employed in conventional machine laundry methods.

In a preferred use aspect a dispensing device is employed in the washing method. The dispensing device is charged with the detergent product, and is used to introduce the product directly into the drum of the washing machine before the commencement of the wash cycle. Its volume capacity should be such as to be able to contain sufficient detergent product as would normally be used in the washing method.

Once the washing machine has been loaded with laundry the dispensing device containing the detergent product is placed inside the drum. At the commencement of the wash cycle of the washing machine water is introduced into the drum and the drum periodically rotates. The design of the dispensing device should be such that it permits containment of the dry detergent product but then allows release of this product during the wash cycle in response to its agitation as the drum rotates and also as a result of its contact with the wash water.

To allow for release of the detergent product during the wash the device may possess a number of openings through which the product may pass. Alternatively, the device

may be made of a material which is permeable to liquid but impermeable to the solid product, which will allow release of dissolved product. Preferably, the detergent product will be rapidly released at the start of the wash cycle thereby providing transient localised high concentrations of product in the drum of the washing machine at this stage of the wash cycle.

Preferred dispensing devices are reusable and are designed in such a way that container integrity is maintained in both the dry state and during the wash cycle.

Alternatively, the dispensing device may be a flexible container, such as a bag or pouch. The bag may be of fibrous construction coated with a water impermeable protective material so as to retain the contents, such as is disclosed in European published Patent Application No. 0018678. Alternatively it may be formed of a water-insoluble synthetic polymeric material provided with an edge seal or closure designed to rupture in aqueous media as disclosed in European published Patent Application Nos. 0011500, 0011501, 0011502, and 0011968. A convenient form of water frangible closure comprises a water soluble adhesive disposed along and sealing one edge of a pouch formed of a water impermeable polymeric film such as polyethylene or polypropylene.

ExamplesAbbreviations used in Examples

In the detergent compositions, the abbreviated component identifications have the following meanings:

STPP	: Sodium tripolyphosphate
Citrate	: Tri-sodium citrate dihydrate
Bicarbonate	: Sodium hydrogen carbonate
Citric Acid	: Anhydrous Citric acid
Carbonate	: Anhydrous sodium carbonate
Silicate	: Amorphous Sodium Silicate (SiO ₂ :Na ₂ O ratio = 1.6-3.2)
PB1	: Anhydrous sodium perborate monohydrate
PB4	: Sodium perborate tetrahydrate of nominal formula NaBO ₂ .3H ₂ O.H ₂ O ₂
Nonionic	: Nonionic surfactant C ₁₃ -C ₁₅ mixed ethoxylated/propoxylated fatty alcohol with an average degree of ethoxylation of 3.8 and an average degree of propoxylation of 4.5, sold under the tradename Plurafac by BASF
TAED	: Tetraacetyl ethylene diamine
HEDP	: Ethane 1-hydroxy-1,1-diphosphonic acid
DETPMP	: Diethyltriamine penta (methylene) phosphonate, marketed by monsanto under the tradename Dequest 2060
PAAC	: Pentaamine acetate cobalt (III) salt
Paraffin	: Paraffin oil sold under the tradename Winog 70 by Wintershall.
Protease	: Proteolytic enzyme
Amylase	: Amylolytic enzyme.
BTA	: Benzotriazole
PA30	: Polyacrylic acid of average molecular weight approximately 4,500
Sulphate	: Anhydrous sodium sulphate.

PEG 4000	:	Polyethylene Glycol molecular weight approximately 4000 available from Hoechst
PEG 8000	:	Polyethylene Glycol molecular weight approximately 8000 available from Hoechst
Sugar	:	Household sucrose
Gelatine	:	Gelatine Type A, 65 bloom strength available from Sigma
Starch	:	modified carboxy methyl cellulose sold under the tradename Nimcel available from metcaserle
Triacetin	:	Glycerin triacetate sold under the tradename available from
Thixatrol	:	Castor oil derivative sold under the tradename Thixatrol sold by Rheox
PVP	:	Poly vinyl pyrrolidone having a molecular weight of 300,000
PEO	:	Polyethylene oxide having a molecular weight of 45,000
pH	:	Measured as a 1% solution in distilled water at 20°C

In the following examples all levels are quoted as % by weight of the compressed portion, the non-compressed portion or the coating layer:

Example 1

The following illustrates examples detergent tablets of the present invention suitable for use in a dishwashing machine.

The compressed portion is prepared by delivering the composition of detergent components to a punch cavity of a modified 12 head rotary tablet press and compressing the composition at a pressure of 13KN/cm². The modified tablet press provides a tablet wherein the compressed portion has a cavity extending from a first external surface of the compressed portion to a second external surface of the compressed portion. The non-compressed portion is poured into the cavity of the compressed portion. For the purposes of Examples A, B and C the non-compressed portion comprises a gelling or binding agent. Once the non-compressed portion has been delivered to the cavity the detergent tablet is subjected to a conditioning step, during which time the non-compressed portion hardens. For the purposes of Examples D and E the non-compressed portion is in

particulate form. In these examples the non-compressed portion is delivered to the compressed portion and is then coated with a coating layer.

	A	B	C	D	E
Compressed portion					
STPP	-	52.0	50.00	55.10	50.00
Citrate	26.40	-	-	-	-
Carbonate	-	16.0	18.40	14.0	18.40
Silicate	26.40	15.0	10.00	14.80	10.00
Protease	-	-	-	-	1.00
Amylase	0.6	0.75	2.0	0.75	2.0
PB1	1.56	12.20	15.70	12.50	15.70
PB4	6.92	-	-	-	-
Nonionic	1.50	1.50	0.80	1.5	0.80
PAAC	-	0.016	-	0.016	-
TAED	4.33	-	1.30	-	1.30
HEDP	0.67	-	-	-	-
DETPMP	0.65	-	-	-	-
Paraffin	0.42	0.5	0.50	0.50	0.50
BTA	0.24	0.3	0.33	0.30	0.33
PA30	3.2	-	-	-	-
Perfume	-	-	0.20	-	0.20
Sulphate	24.05	2.00	10.68	-	10.68
Misc/water to balance					
Weight (g)	20.0g	20.0g	22g	20.0g	20.0g

Non-compressed portion

Protease	7.00	7.00	12.1	8.12	-
Amylase	6.80	9.30	12.4	13.00	8.00
Metasilicate	-	-	-	50.02	40.00
Bicarbonate	16.00	-	-	13.00	6.00
Citric acid	20.00			13.00	6.00
Citrate	-	-	-	-	40.00
PEG 4000	4.00	-	-	-	-

Sugar	-	55.00	58.00		
Gelatine	-	5.00	7.00		
Starch	-	10.00	-		
Water	-	10.00	10.00		
Triacetin	42.00	-	-		
Misc./balance					
Weight (g)	2.5g	2.5g	3.0g	3.0g	2.5g

Coating Layer					
Dodecanoic acid	-	-	-	90.00	-
Starch	-	-	-	10.00	-
PEG	-	-	-		100
Weight (g)	-	-	-	1.00g	0.50g

Total weight (g) of tablet	22.5g	22.5g	25g	24g	23g
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Claims

1. A detergent tablet comprising a compressed portion and a non-compressed portion wherein:
 - a) the compressed portion comprises at least one compressed detergent component and a cavity extending from a first external surface of the compressed portion to a second external surface of the compressed portion; and
 - b) the non-compressed portion is retained within said cavity.
2. A detergent tablet according to claim 1 wherein the compressed portion comprises at least two parallel external surfaces.
3. A detergent tablet according to claim 2 wherein the cavity extends substantially perpendicularly from a first parallel external surface to a second parallel external surface.
4. A detergent tablet according to any of the preceding claims wherein the compressed portion comprises more than one cavity.
5. A detergent tablet according to any of the preceding claims wherein the non-compressed portion comprises a first and a second and optionally subsequent non-compressed portions.
6. A detergent tablet according to any preceding claims wherein the non-compressed portion is in solid, gel or liquid form.
7. A detergent tablet according to any preceding claim wherein the non-compressed portion is retained within the cavity of the compressed portion by coating the non-compressed portion with a coating layer.
8. A detergent tablet according to any preceding claim wherein the compressed portion, the non-compressed portion or the coating layer comprises a disrupting agent which may be for example a disintegrating or effervescent agent.
9. A process for preparing a detergent tablet according to any of the preceding claims comprising the steps of:

- a) compressing detergent components to form a compressed portion having a cavity extending from a first external surface of the compressed portion to a second external surface of the compressed portion; and
- b) delivering a non-compressed portion to said cavity.

INTERNATIONAL SEARCH REPORT

National Application No
PCT/US 98/25075

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D17/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	GB 2 327 949 A (PROCTER & GAMBLE) 10 February 1999 see the whole document	1-9
A	EP 0 224 135 A (HENKEL KGAA) 3 June 1987 cited in the application see page 9, line 33 - line 44; claims; example; tables	1, 6-9
A	EP 0 481 547 A (UNILEVER) 22 April 1992 see claim 1; figures	1-3, 6-9
A	EP 0 481 793 A (UNILEVER) 22 April 1992 see claims	1

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/25075

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
GB 2327949	A 10-02-1999	WO	9906522 A	11-02-1999
EP 0224135	A 03-06-1987	DE	3541147 A	27-05-1987
		CA	1291918 A	12-11-1991
		JP	62129396 A	11-06-1987
		US	4913832 A	03-04-1990
EP 0481547	A 22-04-1992	US	5133892 A	28-07-1992
		CA	2053399 A	18-04-1992
EP 0481793	A 22-04-1992	AU	632713 B	07-01-1993
		AU	8584291 A	25-06-1992
		CA	2053434 A,C	20-04-1992
		DE	69101896 D	09-06-1994
		DE	69101896 T	11-08-1994
		ES	2052337 T	01-07-1994
		JP	2628812 B	09-07-1997
		JP	4285698 A	09-10-1992
		KR	9505384 B	23-05-1995
		ZA	9108338 A	19-04-1993